THE NEET EDGE

Chapterwise Collection of Most Difficult Chemistry Questions asked in last 15 Years' NEET/AIPMT

CHEMISTRY

1. *Some Basic Principles of Chemistry*

1. An element, X has the following isotopic composition :

^{200}X : 90%, ^{199}X : 8.0%, ^{202}X : 2.0%

The weighted average atomic mass of the naturally occurring element X is closest to **[CBSE-AIPMT 2007]**

(a) 201 u (b) 202 u (c) 199 u (d) 200 u

2. If Avogadro number N_A , is changed from 6.022×10^{23} mol^{-1} to 6.022×10^{20} mol^{-1} this would change **[CBSE-AIPMT 2015]**

(a) the definition of mass in units of grams
(b) the mass of one mole of carbon
(c) the ratio of chemical species to each other in a balanced equation
(d) the ratio of elements to each other in a compound

3. In which case is the number of molecules of water maximum? **[NEET 2018]**

(a) 0.00224 L of water vapours at 1 atm and 273 K
(b) 0.18 g of water
(c) 18 mL of water
(d) 10^{-3} moles of water

4. The number of atoms in 0.1 mole of a triatomic gas is ($N_A = 6.023 \times 10^{23}$ mol^{-1}) **[CBSE-AIPMT 2010]**

(a) 6.026×10^{22} (b) 1.806×10^{23}
(c) 3.600×10^{23} (d) 1.800×10^{22}

5. How many grams of concentrated nitric acid solution should be used to prepare 250 mL of 2.0 M HNO_3? The concentrated acid is 70% HNO_3. **[NEET 2013]**

(a) 45.0 g conc. HNO_3 (b) 90.0 g conc. HNO_3
(c) 70.0 g conc. HNO_3 (d) 54.0 g conc. HNO_3

6. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample? (Atomic weight of Mg = 24) **[CBSE-AIPMT 2015]**

(a) 75 (b) 96
(c) 60 (d) 84

7. A mixture of 2.3 g formic acid and 4.5 g oxalic acid is treated with conc. H_2SO_4. The evolved gaseous mixture is passed through KOH pellets. Weight (in g) of the remaining product at STP will be

(a) 2.8 (b) 3.0 **[NEET 2018]**
(c) 1.4 (d) 4.4

8. Number of moles of MnO_4^- required to oxidise one mole of ferrous oxalate completely in acidic medium will be **[CBSE-AIPMT 2008]**

(a) 0.6 mol (b) 0.4 mol
(c) 7.5 mol (d) 0.2 mol

9. The number of moles of $KMnO_4$ reduced by one mole of KI in alkaline medium is **[CBSE-AIPMT 2005]**

(a) one fifth (b) five (c) one (d) two

10. What is the mass of precipitate formed when 50 mL of 16.9% solution of $AgNO_3$ is mixed with 50 mL of 5.8% NaCl solution? (Ag = 107.8, N = 14, O = 16, Na = 23, and Cl = 35.5) **[CBSE-AIPMT 2015]**

(a) 28 g (b) 3.5 g
(c) 7 g (d) 14 g

11. 10 g of hydrogen and 64 g of oxygen were filled in a steel vessel and exploded. Amount of water produced in this reaction will be **[CBSE-AIPMT 2009]**

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

12. How many moles of lead (II) chloride will be formed from a reaction between 6.5 g of PbO and 3.2 g of HCl? **[CBSE-AIPMT 2008]**

(a) 0.044 (b) 0.333 (c) 0.011 (d) 0.029

13. What volume of oxygen gas (O_2) measured at 0°C and 1 atm, is needed to burn completely 1 L of propane gas (C_3H_8) measured under the same conditions? **[CBSE-AIPMT 2008]**

(a) 7 L (b) 6 L (c) 5 L (d) 10 L

14. When 22.4 L of $H_2(g)$ is mixed with 11.2 L of $Cl_2(g)$, each at STP, the moles of HCl (g) formed is equal to **[CBSE-AIPMT 2005]**

(a) 1 mole of HCl (g) (b) 2 moles of HCl (g)
(c) 0.5 mole of HCl (g) (d) 1.5 moles of HCl (g)

15. 1.0 g of magnesium is burnt with 0.56 g of oxygen in a closed vessel. Which reactant is left in excess and how much? (Atomic weight of Mg = 24, O = 16) **[CBSE-AIPMT 2014]**

(a) Mg, 0.16 g (b) O_2, 0.16 g (c) Mg, 0.44 g (d) O_2, 0.28 g

2. *Structure of Atoms*

16. The frequency of radiation emitted when the electron falls from $n = 4$ to $n = 1$ in a hydrogen atom will be (Given ionisation energy of $H = 2.18 \times 10^{-18}$ J atm^{-1} and $h = 6.625 \times 10^{-34}$ Js) **[CBSE-AIPMT 2004]**

(a) $1.54 \times 10^{15}\ s^{-1}$ (b) $1.03 \times 10^{15}\ s^{-1}$
(c) $3.08 \times 10^{15}\ s^{-1}$ (d) $2.00 \times 10^{15}\ s^{-1}$

17. Which one is the wrong statement? **[NEET 2017]**

(a) de-Broglie's wavelength is given by $\lambda = \frac{h}{mv}$, where m = mass of the particle, v = group velocity of the particle
(b) The uncertainty principle is $\Delta E \times \Delta t \geq h / 4\pi$
(c) Half-filled and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement
(d) The energy of $2s$-orbital is less than the energy of $2p$-orbital in case of hydrogen like atoms

18. The value of Planck's constant is 6.63×10^{-34} Js. The speed of light is 3×10^{17} nm s^{-1}. Which value is closest to the wavelength in nanometer of a quantum of light with frequency of $6 \times 10^{15}\ s^{-1}$? **[NEET 2013]**

(a) 10 nm (b) 25 nm
(c) 50 nm (d) 75 nm

19. The measurement of the electron position is associated with an uncertainty in momentum, which is equal to 1×10^{-18} g cm s^{-1}. The uncertainty in electron velocity is (Mass of an electron is 9×10^{-28} g) **[CBSE-AIPMT 2008]**

(a) 1×10^{9} cm s^{-1} (b) 1×10^{6} cm s^{-1}
(c) 1×10^{5} cm s^{-1} (d) 1×10^{11} cm s^{-1}

20. Which of the following is not permissible arrangement of electrons in an atom? **[CBSE-AIPMT 2009]**

(a) $n = 4, l = 0, m = 0, s = -1/2$
(b) $n = 5, l = 3, m = 0, s = +1/2$
(c) $n = 3, l = 2, m = -3, s = -1/2$
(d) $n = 3, l = 2, m = -2, s = -1/2$

21. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers? $n = 3$, $l = 1$ and $m = -1$ **[NEET 2013]**

(a) 10 (b) 6 (c) 4 (d) 2

22. What is the maximum number of orbitals that can be identified with the following quantum numbers? $n = 3$, $l = 1$ and $m_l = 0$ **[CBSE-AIPMT 2014]**

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

23. How many electrons can fit in the orbital for which $n = 3$ and $l = 1$? **[NEET 2016, Phase II]**

(a) 2 (b) 6 (c) 10 (d) 14

24. If $n = 6$, the correct sequence for filling of electrons will be **[CBSE-AIPMT 2011]**

(a) $ns \longrightarrow (n-1)d \longrightarrow (n-2)f \longrightarrow np$
(b) $ns \longrightarrow (n-2)f \longrightarrow np \longrightarrow (n-1)d$
(c) $ns \longrightarrow np \longrightarrow (n-1)d \longrightarrow (n-2)f$
(d) $ns \longrightarrow (n-2)f \longrightarrow (n-1)d \longrightarrow np$

25. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium? **[CBSE-AIPMT 2015]**

(a) $3s, 4s, 3p, 3d$ (b) $4s, 3s, 3p, 3d$
(c) $3s, 3p, 3d, 4s$ (d) $3s, 3p, 4s, 3d$

26. Consider the following sets of quantum numbers.

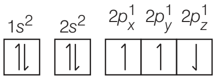
	n	*l*	*m*	*s*
I	3	0	0	+1/2
II	2	2	1	+1/2
III	4	3	–2	–1/2
IV	1	0	–1	–1/2
V	3	2	3	+1/2

Which of the following sets of quantum number is not possible? **[CBSE-AIPMT 2007]**

(a) II, III and IV (b) I, II, III and IV
(c) II, IV and V (d) I and III

27. Which one is a wrong statement? **[NEET 2018]**

(a) The electronic configuration of N-atom is



(b) An orbital is designated by three quantum numbers while an electron in an atom is designated by four quantum numbers
(c) Total orbital angular momentum of electron in 's'-orbital is equal to zero
(d) The value of m for d_{z^2} is zero

3. *Classification of Elements and Periodicity in Properties*

28. The element $Z = 114$ has been discovered recently. It will belong to which of the following family/group and electronic configuration? **[NEET 2017]**

(a) Halogen family, [Rn] $5f^{14}, 6d^{10}, 7s^2, 7p^5$
(b) Carbon family, [Rn] $5f^{14}, 6d^{10}, 7s^2, 7p^2$
(c) Oxygen family, [Rn] $5f^{14}, 6d^{10}, 7s^2, 7p^4$
(d) Nitrogen family, [Rn] $5f^{14}, 6d^{10}, 7s^2, 7p^6$

29. Which of the following orders of ionic radii is correctly represented? **[CBSE-AIPMT 2014]**

(a) $H^- > H^+ > H$
(b) $Na^+ > F^- > O^{2-}$
(c) $F^- > O^{2-} > Na^+$
(d) $Al^{3+} > Mg^{2+} > N^{3-}$

30. Identify the correct order of the size of the following. **[CBSE-AIPMT 2007]**

(a) $Ca^{2+} < K^+ < Ar < S^{2-} < Cl^-$
(b) $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$
(c) $Ar < Ca^{2+} < K^+ < Cl^- < S^{2-}$
(d) $Ca^{2+} < Ar < K^+ < Cl^- < S^{2-}$

31. Identify the wrong statement in the following. **[CBSE-AIPMT 2012]**

(a) Amongst isoelectronic species, smaller the positive charge on the cation, smaller is the ionic radius
(b) Amongst isoelectronic species, greater the negative charge on the anion, larger is the ionic radius
(c) Atomic radius of the elements increases as one moves down the first group of the periodic table
(d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table

32. The correct order of decreasing second ionisation enthalpy of Ti(22), V(23), Cr(24) and Mn(25) is **[CBSE-AIPMT 2008]**

(a) Cr > Mn > V > Ti
(b) V > Mn > Cr > Ti
(c) Mn > Cr > Ti > V
(d) Ti > V > Cr > Mn

33. Which of the following represents the correct order of increasing electron gain enthalpy with negative sign for the elements O, S, F and Cl? **[CBSE-AIPMT 2010]**

(a) Cl< F< O< S
(b) O< S< F< Cl
(c) F< S< O< Cl
(d) S< O< Cl< F

34. In which of the following options the order of arrangement does not agree with the variation of property indicated against it? **[NEET 2016, Phase I]**

(a) B < C < N < O (increasing first ionisation enthalpy)
(b) I < Br < Cl < F (increasing electron gain enthalpy)
(c) Li < Na < K < Rb (increasing metallic radius)
(d) $Al^{3+} < Mg^{2+} < Na^+ < F^-$ (increasing ionic size)

35. Which of the following oxides is not expected to react with sodium hydroxide? **[CBSE-AIPMT 2009]**

(a) B_2O_3
(b) CaO
(c) SiO_2
(d) BaO

4. *Chemical Bonding and Molecular Structure*

36. The hybridisations of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ respectively are **[NEET 2016, Phase II]**

(a) *sp*, sp^3 and sp^2
(b) sp^2, sp^3 and *sp*
(c) *sp*, sp^2 and sp^3
(d) sp^2, *sp* and sp^3

37. In which one of the following species the central atom has the type of hybridisation which is not the same as that present in the other three? **[CBSE-AIPMT 2010]**

(a) SF_4
(b) I_3^-
(c) $SbCl_5^{2-}$
(d) PCl_5

38. The correct order of increasing bond angles in the following species is **[CBSE-AIPMT 2010]**

(a) $Cl_2O < ClO_2 < ClO_2^-$
(b) $ClO_2 < Cl_2O < ClO_2^-$
(c) $Cl_2O < ClO_2^- < ClO_2$
(d) $ClO_2^- < Cl_2O < ClO_2$

39. Which of the following species contains three bond pairs and one lone pair around the central atom? **[NEET 2013]**

(a) H_2O
(b) BF_3
(c) NH_2^-
(d) PCl_3

40. The electronegativity difference between N and F is greater than that between N and H yet the dipole moment of NH_3 (1.5 D) is larger than that of NF_3 (0.2 D). This is because **[CBSE-AIPMT 2006]**

(a) in NH_3 as well as in NF_3, the atomic dipole and bond dipole are in the same direction
(b) in NH_3, the atomic dipole and bond dipole are in the same direction whereas in NF_3 these are in opposite directions
(c) in NH_3 as well as NF_3, the atomic dipole and bond dipole are in opposite directions
(d) in NH_3 the atomic dipole and bond dipole are in the opposite directions whereas in NF_3 these are in the same directions

41. In BrF_3 molecule, the lone pairs occupy equatorial positions to minimise **[CBSE-AIPMT 2004]**

(a) lone pair-bond pair repulsion
(b) bond pair-bond pair repulsion
(c) lone pair-lone pair repulsion and lone pair-bond pair repulsion
(d) lone pair-lone pair repulsion

42. Which of the following is paramagnetic? **[NEET 2013]**

(a) CO
(b) O_2^-
(c) CN^-
(d) NO^+

43. Which one of the following species does not exist under normal conditions? **[CBSE-AIPMT 2010]**

(a) Be_2^+
(b) Be_2
(c) B_2
(d) Li_2

44. According to molecular orbital theory which of the following lists rank the nitrogen species in terms of increasing bond order? **[CBSE-AIPMT 2009]**

(a) $N_2^- < N_2 < N_2^{2-}$
(b) $N_2^{2-} < N_2^- < N_2$
(c) $N_2 < N_2^{2-} < N_2^-$
(d) $N_2^- < N_2^{2-} < N_2$

45. Four diatomic species are listed below in different sequences. Which of these presents the correct order of their increasing bond order? **[CBSE-AIPMT 2008]**

(a) $O_2^- < NO < C_2^{2-} < He_2^+$
(b) $NO < C_2^{2-} < O_2^- < He_2^+$
(c) $C_2^{2-} < He_2^+ < NO < O_2^-$
(d) $He_2^+ < O_2^- < NO < C_2^{2-}$

5. *States of Matter*

46. A 20 L container at 400 K contains $CO_2(g)$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be **[NEET 2017]**

(Given that :

$$SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g) ; K_p = 1.6 \text{ atm})$$

(a) 5 L (b) 10 L (c) 4 L (d) 2 L

47. Equal masses of H_2, O_2 and methane have been taken in a container of volume V at temperature 27°C in identical conditions. The ratio of the volumes of gases $H_2 : O_2 : CH_4$ would be **[CBSE-AIPMT 2014]**

(a) 8 : 16 : 1
(b) 16 : 8 : 1
(c) 16 : 1 : 2
(d) 8 : 1 : 2

48. A gaseous mixture was prepared by taking equal moles of CO and N_2. If the total pressure of the mixture was found 1 atm, the partial pressure of the nitrogen (N_2) in the mixture is **[CBSE-AIPMT 2011]**

(a) 0.8 atm (b) 0.9 atm (c) 1 atm (d) 0.5 atm

49. Equal moles of hydrogen and oxygen gases are placed in container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape? **[NEET 2016, Phase I]**

(a) 1/4 (b) 3/8 (c) 1/2 (d) 1/8

50. 50 mL of each gas A and of gas B takes 150 and 200 s respectively for effusing through a pin-hole under the similar conditions. If molecular mass of gas B is 36, the molecular mass of gas A will be

(a) 96
(b) 128 **[CBSE-AIPMT 2012]**
(c) 32
(d) 64

51. By what factor does the average velocity of a gaseous molecule increase when the temperature (in Kelvin) is doubled? **[CBSE-AIPMT 2011]**

(a) 2.8 (b) 4.0 (c) 1.4 (d) 2.0

52. Maximum deviation from ideal gas is expected from **[NEET 2013]**

(a) $H_2(g)$
(b) $N_2(g)$
(c) $CH_4(g)$
(d) $NH_3(g)$

6. *Thermodynamics*

53. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be **[NEET 2017]**

(a) 1136.25 J
(b) – 500 J
(c) – 505 J
(d) + 505 J

54. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm, is **[CBSE-AIPMT 2004]**

(a) – 6 J
(b) – 608 J
(c) + 304 J
(d) – 304 J

55. The heat of combustion of carbon to CO_2 is –393.5 kJ / mol. The heat released upon the formation of 35.2 g of CO_2 from carbon and oxygen gas is **[CBSE-AIPMT 2015]**

(a) –315 kJ (b) +315 kJ (c) –630 kJ (d) –3.15 kJ

56. Standard enthalpy of vaporisation $\Delta_{vap}H^\circ$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is (assume water vapour to behave like an ideal gas). **[CBSE-AIPMT 2012]**

(a) + 37.56
(b) – 43.76
(c) + 43.76
(d) + 40.66

57. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1 . ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be **[NEET 2018]**

(a) 800 kJ mol^{-1}
(b) 100 kJ mol^{-1}
(c) 200 kJ mol^{-1}
(d) 400 kJ mol^{-1}

58. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f, the entropy change is given by **[NEET 2016, Phase II]**

(a) $\Delta S = nR \ln\left(\frac{p_f}{p_i}\right)$
(b) $\Delta S = nR \ln\left(\frac{p_i}{p_f}\right)$
(c) $\Delta S = nRT \ln\left(\frac{p_f}{p_i}\right)$
(d) $\Delta S = RT \ln\left(\frac{p_i}{p_f}\right)$

59. For a given reaction, ΔH = 35.5 kJ mol^{-1} and ΔS = 83.6 JK^{-1} mol^{-1}. The reaction is spontaneous at (Assume that ΔH and ΔS do not vary with temperature) **[NEET 2017]**

(a) $T < 425$ K
(b) $T > 425$ K
(c) all temperatures
(d) $T > 298$ K

60. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is **[NEET 2016, Phase I]**

(a) $\Delta H > 0$ and $\Delta S < 0$
(b) $\Delta H < 0$ and $\Delta S > 0$
(c) $\Delta H < 0$ and $\Delta S < 0$
(d) $\Delta H < 0$ and $\Delta S = 0$

61. Consider the following liquid-vapour equilibrium :

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

Which of the following relations is correct? **[NEET 2016, Phase I]**

(a) $\frac{d\ln p}{dT} = \frac{-\Delta H_v}{RT}$ (b) $\frac{d\ln p}{dT^2} = \frac{-\Delta H_v}{T^2}$

(c) $\frac{d\ln p}{dT} = \frac{-\Delta H_v}{RT^2}$ (d) $\frac{d\ln G}{dT^2} = \frac{-\Delta H_v}{RT^2}$

7. *Equilibrium*

62. If the value of an equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain **[CBSE-AIPMT 2015]**

(a) all reactants

(b) mostly reactants

(c) mostly products

(d) similar amounts of reactants and products

63. The equilibrium constants of the following are

$$N_2 + 3H_2 \rightleftharpoons 2NH_3;\ K_1$$

$$N_2 + O_2 \rightleftharpoons 2NO;\ K_2$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O;\ K_3$$

The equilibrium constant (K) of the reaction

$$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O, \text{ will be}$$

[NEET 2017, CBSE-AIPMT 2007]

(a) $K_1K_3^3/K_2$ (b) $K_2K_3^3/K_1$

(c) K_2K_3/K_1 (d) $K_2^3K_3/K_1$

64. If the concentration of OH^- ions in the reaction, $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by **[CBSE-AIPMT 2008]**

(a) 8 times (b) 16 times (c) 64 times (d) 4 times

65. The dissociation equilibrium of a gas AB_2 can be represented as

$$2\,AB_2(g) \rightleftharpoons 2\,AB(g) + B_2(g)$$

The degree of dissociation is x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure p is **[CBSE-AIPMT 2008]**

(a) $(2K_p/p)$ (b) $(2K_p/p)^{1/3}$

(c) $(2K_p/p)^{1/2}$ (d) (K_p/p)

66. The value of ΔH for the reaction, $X_2(g) + 4Y_2(g) \rightleftharpoons 2XY_4(g)$ is less than zero. Formation of $XY_4(g)$ will be favoured at **[CBSE-AIPMT 2011]**

(a) low pressure and low temperature

(b) high temperature and low pressure

(c) high pressure and low temperature

(d) high temperature and high pressure

67. Which of the following fluoro-compounds is most likely to behave as a Lewis base? **[NEET 2016, Phase II]**

(a) BF_3 (b) PF_3 (c) CF_4 (d) SiF_4

68. The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10}, respectively. The equilibrium constant for the equilibrium, $CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ would be **[CBSE-AIPMT 2009]**

(a) 3.0×10^{5} (b) 3.0×10^{-5} (c) 3.0×10^{-4} (d) 3.0×10^{4}

69. The percentage of pyridine (C_5H_5N) that forms pyridinium ion ($C_5H_5N^+H$) in a 0.10 M aqueous pyridine solution (K_b for $C_5H_5N = 1.7 \times 10^{-9}$) is **[NEET 2016, Phase II]**

(a) 0.0060% (b) 0.013% (c) 0.77% (d) 1.6%

70. Which of the following salts will give highest pH in water? **[CBSE-AIPMT 2014]**

(a) KCl (b) NaCl (c) Na_2CO_3 (d) $CuSO_4$

71. Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations :

I. $60\text{ mL}\frac{M}{10}\text{ HCl} + 40\text{ mL}\frac{M}{10}\text{ NaOH}$

II. $55\text{ mL}\frac{M}{10}\text{ HCl} + 45\text{ mL}\frac{M}{10}\text{ NaOH}$

III. $75\text{ mL}\frac{M}{5}\text{ HCl} + 25\text{ mL}\frac{M}{5}\text{ NaOH}$

IV. $100\text{ mL}\frac{M}{10}\text{ HCl} + 100\text{ mL}\frac{M}{10}\text{ NaOH}$

pH of which one of them will be equal to 1? **[NEET 2018]**

(a) IV (b) I (c) II (d) III

72. The ionisation constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is **[CBSE-AIPMT 2009]**

(a) 5.65×10^{-10} (b) 6.50×10^{-12}

(c) 5.65×10^{-13} (d) 5.65×10^{-12}

73. The solubility of $BaSO_4$ in water is 2.42×10^{-3} g L^{-1} at 298 K. The value of its solubility product (K_{sp}) will be

(Given, molar mass of $BaSO_4$ = 233 g mol^{-1}) **[NEET 2018]**

(a) 1.08×10^{-14} mol^2L^{-2} (b) 1.08×10^{-12} mol^2L^{-2}

(c) 1.08×10^{-10} mol^2L^{-2} (d) 1.08×10^{-8} mol^2L^{-2}

74. Using the Gibbs energy change, $\Delta G° = +63.3$ kJ for the following reaction,

$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$ the K_{sp} of $Ag_2CO_3(s)$ in water at 25°C is ($R = 8.314$ $JK^{-1}mol^{-1}$). **[CBSE-AIPMT 2014]**

(a) 3.2×10^{-26} (b) 8.0×10^{-12} (c) 2.9×10^{-3} (d) 7.9×10^{-2}

8. *Redox Reactions*

75. For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients of the reactants for the balanced equation are **[NEET 2018]**

	MnO_4^-	$C_2O_4^{2-}$	H^+		MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	16	5	(b)	2	5	16
(c)	16	5	2	(d)	5	16	2

76. Which of the following does not give oxygen on heating? **[NEET 2013]**

(a) $Zn(ClO_3)_2$ (b) $K_2Cr_2O_7$ (c) $(NH_4)_2Cr_2O_7$ (d) $KClO_3$

77. Which one of the following compounds is a peroxide? **[CBSE-AIPMT 2018]**

(a) KO_2 (b) BaO_2 (c) NO_2 (d) MnO_2

78. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from **[CBSE-AIPMT 2012]**

(a) 0 to +1 and 0 to −3 (b) 0 to −1 and 0 to + 3
(c) 0 to +1 and 0 to − 5 (d) 0 to −1 and 0 to + 5

79. $KMnO_4$ can be prepared from K_2MnO_4 as per the reaction,

$$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$$

The reaction can go to completion by removing OH^- ions by adding **[NEET 2013]**

(a) KOH (b) HCl (c) CO_2 (d) SO_2

9. *Hydrogen*

80. Which of the following statements about hydrogen is incorrect? **[NEET 2016, Phase I]**

(a) Hydrogen never acts as cation in ionic salts
(b) Hydronium ion, H_3O^+ exists freely in solution
(c) Dihydrogen does not act as a reducing agent
(d) Hydrogen has three isotopes of which tritium is the most common

81. I. $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
II. $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$

Role of hydrogen peroxide in the above reaction is respectively **[CBSE-AIPMT 2018]**

(a) reducing in I and oxidising in II
(b) oxidising in I and reducing in II
(c) oxidising in I and II
(d) reducing in I and II

10. *s-block Elements*

82. The sequence of ionic mobility in aqueous solution is **[CBSE-AIPMT 2008]**

(a) $K^+ > Na^+ > Rb^+ > Cs^+$ (b) $Cs^+ > Rb^+ > K^+ > Na^+$
(c) $Rb^+ > K^+ > Cs^+ > Na^+$ (d) $Na^+ > K^+ > Rb^+ > Cs^+$

83. The alkali metals form salt like hydrides by the direct synthesis at elevated temperature. The thermal stability of these hydrides decreases in which of the following orders? **[CBSE-AIPMT 2008]**

(a) CsH > RbH > KH > NaH > LiH
(b) KH > NaH > LiH > CsH > RbH
(c) NaH > LiH > KH > RbH > CsH
(d) LiH > NaH > KH > RbH > CsH

84. "Metals are usually not found as nitrates in their ores". Out of the following two (I and II) reasons which is/are true for the above observation?

I. Metal nitrates are highly unstable.
II. Metal nitrates are highly soluble in water.

[CBSE-AIPMT 2015]

(a) I and II are true (b) I and II are false
(c) I is false but II is true (d) I is true but II is false

85. Among CaH_2, BeH_2, BaH_2, the order of ionic character is **[NEET 2018]**

(a) $BeH_2 < BaH_2 < CaH_2$ (b) $CaH_2 < BeH_2 < BaH_2$
(c) $BeH_2 < CaH_2 < BaH_2$ (d) $BaH_2 < BeH_2 < CaH_2$

86. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest pH? **[CBSE-AIPMT 2008]**

(a) $SrCl_2$ (b) $BaCl_2$
(c) $MgCl_2$ (d) $CaCl_2$

87. Solubility of the alkaline earth's metal sulphates in water decreases in the sequence **[CBSE-AIPMT 2015]**

(a) Mg> Ca> Sr> Ba (b) Ca> Sr> Ba> Mg
(c) Sr> Ca> Mg> Ba (d) Ba> Mg> Sr> Ca

88. In which of the following the hydration energy is higher than the lattice energy? **[CBSE-AIPMT 2007]**

(a) $BaSO_4$ (b) $MgSO_4$
(c) $RaSO_4$ (d) $SrSO_4$

89. The product obtained as a result of a reaction of nitrogen with CaC_2 is **[NEET 2016, Phase I]**

(a) CaCN (b) $CaCN_3$
(c) Ca_2CN (d) $Ca(CN)_2$

90. A solid compound X on heating gives CO_2 gas and a residue. The residue mixed with water forms Y. On passing an excess of CO_2 through Y in water, a clear solution Z is obtained. On boiling Z, compound X is reformed. The compound X is

(a) $Ca(HCO_3)_2$ (b) $CaCO_3$ **[CBSE-AIPMT 2004]**
(c) Na_2CO_3 (d) K_2CO_3

11. *Some p-block Elements*

91. The correct order of atomic radii in group 13 elements is **[NEET 2018]**

(a) B < Ga < Al < Tl < In (b) B < Al < Ga < In < Tl
(c) B < Al < In < Ga < Tl (d) B < Ga < Al < In < Tl

92. The tendency of BF_3, BCl_3 and BBr_3 behave as Lewis acid decreases in the sequence **[CBSE-AIPMT 2009]**

(a) $BCl_3 > BF_3 > BBr_3$ (b) $BBr_3 > BCl_3 > BF_3$
(c) $BBr_3 > BF_3 > BCl_3$ (d) $BF_3 > BCl_3 > BBr_3$

93. Al_2O_3 can be converted into anhy. $AlCl_3$ by heating **[CBSE-AIPMT 2006]**

(a) Al_2O_3 with HCl gas
(b) Al_2O_3 with NaCl in solid state
(c) a mixture of Al_2O_3 and carbon in dry Cl_2 gas
(d) Al_2O_3 with Cl_2 gas

94. AlF_3 is soluble in HF only in presence of KF. It is due to the formation of **[NEET 2016, Phase II]**

(a) $K_3[AlF_3H_3]$ (b) $K_3[AlF_6]$ (c) AlH_3 (d) $K[AlF_3H]$

95. Boric acid is an acid because its molecule **[NEET 2016, Phase II]**

(a) contains replaceable H^+ ion
(b) gives up a proton
(c) accepts OH^- from water releasing proton
(d) combines with proton from water molecule

96. It is because of inability of ns^2 electrons of the valence shell to participate in bonding that **[NEET 2017]**

(a) Sn^{2+} is reducing while Pb^{4+} is oxidising
(b) Sn^{2+} is oxidising while Pb^{4+} is reducing
(c) Sn^{2+} and Pb^{2+} are both oxidising and reducing
(d) Sn^{4+} is reducing while Pb^{4+} is oxidising

97. Name the type of the structure of silicate in which one oxygen atom of $[SiO_4]^{4-}$ is shared? **[CBSE-AIPMT 2011]**

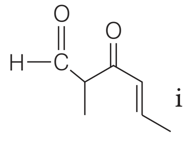
(a) Sheet silicate (b) Pyrosilicate
(c) Three dimensional silicate (d) Linear chain silicate

98. The straight chain polymer is formed by **[CBSE-AIPMT 2009]**

(a) hydrolysis of $(CH_3)_3SiCl$ followed by condensation polymerisation
(b) hydrolysis of CH_3SiCl_3 followed by condensation polymerisation
(c) hydrolysis of $(CH_3)_4Si$ by addition polymerisation
(d) hydrolysis of $(CH_3)_2SiCl_2$ followed by condensation polymerisation

12. *Organic Chemistry : Some Basic Principles and Techniques*

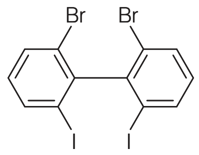
99. The IUPAC name of the compound **[NEET 2017]**

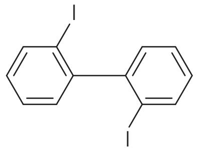


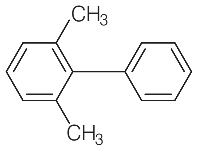
is ....

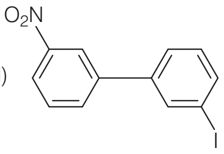
(a) 3-keto-2-methylhex-4-enal (b) 5-formylhex-2-en-3-one
(c) 5-methyl-4-oxohex-2-en-5-al (d) 3-keto-2-methylhex-5-enal

100. Which of the following biphenyls is optically active? **[NEET 2016, Phase I]**

(a)


(b)


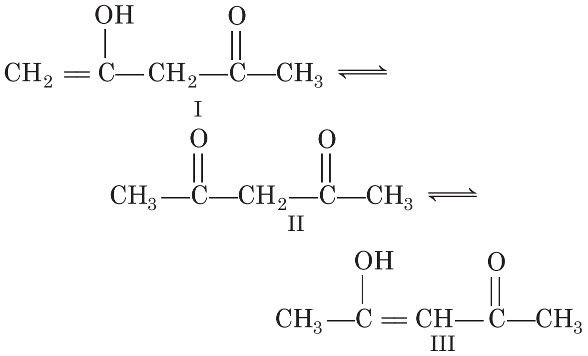
(c)


(d)


101. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is **[NEET 2016, Phase I]**

(a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration
(b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
(c) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
(d) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol

102. The order of stability of the following tautomeric compound is **[NEET 2013]**



$$CH_2=\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons$$
I

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons$$
II

$$CH_3-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$
III

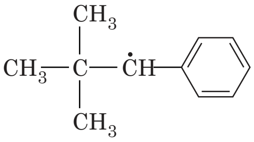
(a) I > II > III (b) III > II > I
(c) II > I> III (d) II > III > I

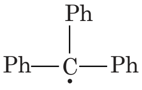
103. How many stereoisomers does this molecule have? **[CBSE-AIPMT 2008]**

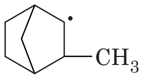
$CH_3CH=CHCH_2CHBrCH_3$

(a) 4 (b) 6
(c) 8 (d) 2

104. Consider the following compounds

I. 

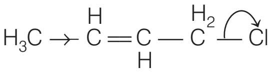
II. 

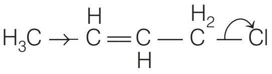
III. 

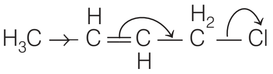
hyperconjugation occurs in **[CBSE-AIPMT 2015]**

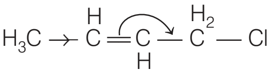
(a) I only (b) II only
(c) III only (d) I and III

105. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? **[CBSE-AIPMT 2015]**

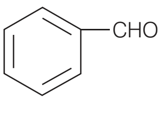
(a) 
$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H_2}{C}-Cl$

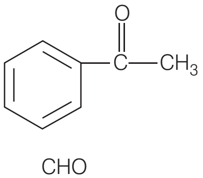
(b) 
$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H_2}{C}-Cl$

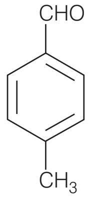
(c) 
$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H_2}{C}-Cl$

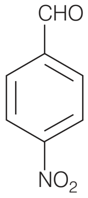
(d) 
$H_3C \rightarrow \overset{H}{C}=\underset{H}{C}-\overset{H_2}{C}-Cl$

106. Which one is most reactive towards nucleophilic addition reaction? **[CBSE-AIPMT 2014]**

(a) 

(c) 

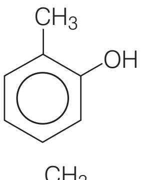
(c) 

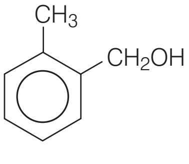
(d) 

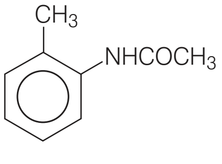
107. Among the following compound one that is most reactive towards electrophilic nitration is **[CBSE-AIPMT 2012]**

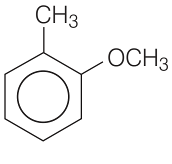
(a) benzoic acid (b) nitrobenzene
(c) toluene (d) benzene

108. Which one is most reactive towards electrophilic reagent ? **[CBSE-AIPMT 2010]**

(a) 

(c) 

(c) 

(d) 

13. *Hydrocarbons*

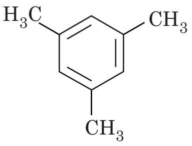
109. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is **[NEET 2016, Phase I]**

(a) the eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain
(b) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
(c) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
(d) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain

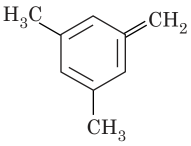
110. Hydrocarbon (*A*) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms. *A* is **[NEET 2018]**

(a) CH_3-CH_3 (b) $CH_2=CH_2$ (c) $CH\equiv CH$ (d) CH_4

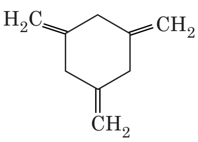
111. Given,



I



II

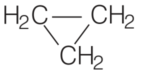


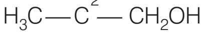
III

The enthalpy of hydrogenation of these compounds will be in the order as **[CBSE-AIPMT 2015]**

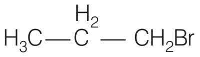
(a) I > II > III (b) III > II > I (c) II > III > I (d) II > I > III

112. Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction? **[NEET 2016, Phase II]**

(a) 

(b) 
$H_3C-\overset{H_2}{C}-CH_2OH$

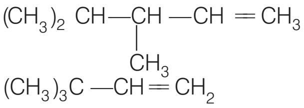
(c) $H_2C=C=O$

(d) 
$H_3C-\overset{H_2}{C}-CH_2Br$

113. Reaction of HBr with propene in the presence of peroxide gives **[CBSE-AIPMT 2004]**

(a) *iso*-propyl bromide (b) 3-bromopropane
(c) allyl bromide (d) *n*-propyl bromide

114. 2,3-dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid? **[NEET 2016, Phase I]**

(a) 
$(CH_3)_2\,CH-\underset{CH_3}{CH}-CH=CH_3$

(b) $(CH_3)_3C-CH=CH_2$
(c) $(CH_3)_2C=CH-CH_2-CH_2$
(d) $(CH_3)_2CH-CH_2-CH=CH_2$

115. Which one is the correct order of acidity? **[NEET 2017]**

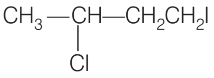
(a) $CH_2 = CH_2 > CH_3—CH = CH_2 > CH_3—C \equiv CH > CH \equiv CH$
(b) $CH \equiv CH > CH_3—C \equiv CH > CH_2 = CH_2 > CH_3—CH_3$
(c) $CH \equiv CH > CH_2 = CH_2 > CH_3—C \equiv CH > CH_3—CH_3$
(d) $CH_3—CH_3 > CH_2 = CH_2 > CH_3—C \equiv CH > CH \equiv CH$

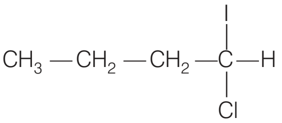
116. In the reaction, $H—C \equiv CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq.}NH_3} X \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq.}NH_3} Y$, X and Y are **[NEET 2016, Phase I]**

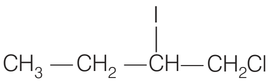
(a) X = 2-butyne; Y = 3-hexyne
(b) X = 2-butyne; Y = 2-hexyne
(c) X = 1-butyne; Y = 2-hexyne
(d) X = 1-butyne; Y = 3-hexyne

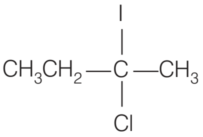
117. Predict the product C obtained in the following reaction of butyne-1. **[CBSE-AIPMT 2007]**

$$CH_3CH_2—C \equiv CH + HCl \longrightarrow B \xrightarrow{HI} C$$

(a) 
$CH_3—\underset{\underset{Cl}{|}}{CH}—CH_2CH_2I$

(b) 
$CH_3—CH_2—CH_2—\overset{\overset{I}{|}}{\underset{\underset{Cl}{|}}{C}}—H$

(c) 
$CH_3—CH_2—\overset{\overset{I}{|}}{CH}—CH_2Cl$

(d) 
$CH_3CH_2—\overset{\overset{I}{|}}{\underset{\underset{Cl}{|}}{C}}—CH_3$

118. Which of the following can be used as the halide component for Friedel-Crafts reaction? **[NEET 2016, Phase II]**

(a) Chlorobenzene
(b) Bromobenzene
(c) Chloroethene
(d) Isopropyl chloride

119. The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are **[CBSE-AIPMT 2010]**

(a) X = benzal chloride, Y = *o*-chlorotoluene
(b) X = *m*-chlorotoluene, Y = *p*-chlorotoluene
(c) X = *o* and *p*-chlorotoluene, Y = trichloromethyl benzene
(d) X = benzyl chloride, Y = *m*-chlorotoluene

14. *Environmental Chemistry*

120. Which of the following is a sink for CO? **[NEET 2017]**

(a) Haemoglobin
(b) Microorganisms present in the soil
(c) Oceans
(d) Plants

121. Which one of the following is not a common component of photochemical smog? **[CBSE-AIPMT 2014]**

(a) Ozone
(b) Acrolein
(c) Peroxyacetyl nitrate
(d) Chlorofluorocarbons

122. Which one of the following statements is not true? **[CBSE-AIPMT 2011]**

(a) Clean water would have a BOD value of less than 5 ppm
(b) Concentration of DO below 6 ppm is good for the growth of fish
(c) pH of drinking water should be between 5.5-9.5
(d) Oxides of sulphur, nitrogen and carbon are the most wide spread air pollutant

123. Which oxide of nitrogen is not a common pollutant introduced into the atmosphere both due to natural and human activity? **[NEET 2018]**

(a) NO (b) NO_2 (c) N_2O_5 (d) N_2O

15. *Solid State*

124. In calcium fluoride, having the fluorite structure, the coordination numbers for calcium ion (Ca^{2+}) and fluoride ion (F^-) are **[NEET 2016, Phase II]**

(a) 4 and 2
(b) 6 and 6
(c) 8 and 4
(d) 4 and 8

125. Which one of the following statements is an incorrect? **[CBSE-AIPMT 2008]**

(a) The fraction of the total volume occupied by the atoms in a primitive cell is 0.48
(b) Molecular solids are generally volatile
(c) The number of carbon atoms in an unit cell of diamond is 4
(d) The number of Bravais lattices in which a crystal can be categorised is 14

126. Percentage of free space in body centred cubic (bcc) unit cell is **[CBSE-AIPMT 2008]**

(a) 30% (b) 32% (c) 34% (d) 28%

127. If 'a' stands for the edge length of the cubic systems : simple cubic, body centred cubic and face centred cubic, then the ratio of radii of the spheres in these systems will be respectively, **[CBSE-AIPMT 2008]**

(a) $\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$
(b) $\frac{1}{2}a : \sqrt{3}a : \frac{1}{\sqrt{2}}a$
(c) $\frac{1}{2}a : \frac{\sqrt{3}}{2}a : \frac{\sqrt{2}}{2}a$
(d) $1a : \sqrt{3}a : \sqrt{2}a$

128. Iron exhibits bcc structure at room temperature. Above 900°C, it transforms to fcc structure. The ratio of density of iron at room temperature to that at 900°C (assuming molar mass and atomic radii of iron remains constant with temperature) is

(a) $\frac{3\sqrt{3}}{4\sqrt{2}}$ (b) $\frac{4\sqrt{3}}{3\sqrt{2}}$ (c) $\frac{\sqrt{3}}{\sqrt{2}}$ (d) $\frac{1}{2}$

129. Lithium has a bcc structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of lithium metal. ($N_A = 6.02 \times 10^{23}\ mol^{-1}$) **[NEET 2016, Phase I]**

(a) 352 pm (b) 527 pm (c) 264 pm (d) 154 pm

130. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is **[NEET 2016, Phase I]**

(a) 4 (b) 8 (c) 2 (d) 6

131. Which is the incorrect statement? **[NEET 2017]**

(a) $FeO_{0.98}$ has non-stoichiometric metal deficiency defect
(b). Density decreases in case of crystals with Schottky's defect
(c) NaCl(s) is insulator, silicon is semiconductor, silver is conductor, quartz is piezoelectric crystal
(d) Frenkel defect is favoured in those ionic compounds in which sizes of cation and anions are almost equal

132. If NaCl is doped with 10^{-4} mol % of $SrCl_2$, the concentration of cation vacancies will be ($N_A = 6.023 \times 10^{23}\, mol^{-1}$) **[CBSE-AIPMT 2007]**

(a) $6.023 \times 10^{15}\, mol^{-1}$ (b) $6.023 \times 10^{16}\, mol^{-1}$
(c) $6.023 \times 10^{17}\, mol^{-1}$ (d) $6.023 \times 10^{14}\, mol^{-1}$

16. *Solutions*

133. A solution has 1 : 4 mole ratio of pentane to hexane. The vapour pressure of the pure hydrocarbons at 20°C are 440 mm of Hg for pentane and 120 mm of Hg for hexane. The mole fraction of pentane in the vapour phase would be **[CBSE-AIPMT 2005]**

(a) 0.549 (b) 0.200 (c) 0.786 (d) 0.478

134. If molality of the dilute solution is doubled, the value of molal depression constant (K_f) will be **[NEET 2017]**

(a) doubled (b) halved
(c) tripled (d) unchanged

135. 25.3 g of sodium carbonate, Na_2CO_3 is dissolved in enough water to make 250 mL of solution. If sodium carbonate dissociates completely, molar concentration of sodium ion, Na^+ and carbonate ion, CO_3^{2-} are respectively (molar mass of $Na_2CO_3 = 106\, g\, mol^{-1}$) **[CBSE-AIPMT 2010]**

(a) 0.955 M and 1.910 M (b) 1.910 M and 0.955 M
(c) 1.90 M and 1.910 M (d) 0.477 M and 0.477 M

136. An aqueous solution is 1.00 molal in KI. Which change will cause the vapour pressure of the solution to increase? **[CBSE-AIPMT 2010]**

(a) Addition of NaCl (b) Addition of Na_2SO_4
(c) Addition of 1.00 molal KI (d) Addition of water

137. Which of the following statements about the composition of the vapour over an ideal 1:1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C.
(Given, vapour pressure data at 25°C, benzene = 12.8 kPa, toluene = 3.85 kPa) **[NEET 2016, Phase I]**

(a) The vapour will contain a higher percentage of toluene
(b) The vapour will contain equal amounts of benzene and toluene
(c) Not enough information is given to make a prediction
(d) The vapour will contain a higher percentage of benzene

138. At 100°C the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If $K_b = 0.52$, the boiling point of this solution will be **[NEET 2016, Phase I]**

(a) 100°C (b) 102°C (c) 103°C (d) 101°C

139. The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolal solution of Y in water. Which one of the following statements is true in this case? **[CBSE-AIPMT 2015]**

(a) X is undergoing dissociation in water
(b) Molecular mass of X is greater than the molecular mass of Y
(c) Molecular mass of X is less than the molecular mass of Y
(d) Y is undergoing dissociation in water while X undergoes no change

140. Which one of the following electrolytes has the same value of van't Hoff factor (i) as that of $Al_2(SO_4)_3$ (if all are 100% ionised)? **[CBSE-AIPMT 2015]**

(a) K_2SO_4 (b) $K_3[Fe(CN)_6]$
(c) $Al(NO_3)_3$ (d) $K_4[Fe(CN)_6]$

141. The freezing point depression constant for water is – 1.86°C m^{-1}. If 5.00 g Na_2SO_4 is dissolved in 45.0 g H_2O, the freezing point is changed by – 3.82°C. Calculate the van't Hoff factor for Na_2SO_4. **[CBSE-AIPMT 2011]**

(a) 2.63 (b) 3.11 (c) 0.381 (d) 2.05

142. A solution of sucrose (molar mass = 342 g mol^{-1}) has been prepared by dissolving 68.5 g of sucrose in 1000 g of water. The freezing point of the solution obtained will be (k_f for water = 1.86 K kg mol^{-1}) **[CBSE-AIPMT 2010]**

(a) – 0.372°C (b) – 0.520°C
(c) + 0.372°C (d) – 0.570°C

143. A 0.0020 m aqueous solution of an ionic compound $Co(NH_3)_5(NO_2)Cl$ freezes at – 0.00732°C. Number of moles of ions which 1 mole of ionic compound produces on being dissolved in water will be ($k_f = -1.86°\,C/m$) **[CBSE-AIPMT 2009]**

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

144. A solution containing 10 g per dm^3 of urea (molecular mass = 60 g mol^{-1}) is isotonic with a 5% solution of a non-volatile solute. The molecular mass of this non-volatile solute is **[NEET 2006]**

(a) 250 g mol^{-1} (b) 300 g mol^{-1}
(c) 350 g mol^{-1} (d) 200 g mol^{-1}

145. The vapour pressure of two liquids P and Q are 80 and 60 torr, respectively. The total vapour pressure of solution obtained by mixing 3 moles of P and 2 moles of Q would be **[CBSE-AIPMT 2005]**

(a) 140 torr (b) 20 torr (c) 68 torr (d) 72 torr

17. *Electrochemistry*

146. The molar conductivity of a 0.5 mol/dm^3 solution of $AgNO_3$ with electrolytic conductivity of 5.76×10^{-3} S cm^{-1} at 298 K is **[CBSE-AIPMT 2016, Phase II]**

(a) 2.88 S cm^2/mol (b) 11.52 S cm^2/mol
(c) 0.086 S cm^2/mol (d) 28.8 S cm^2/mol

147. At 25° C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 Ω^{-1} cm^2 mol^{-1} and at infinite dilution its molar conductance is 238 Ω^{-1} cm^2 mol^{-1}. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is **[NEET 2013]**

(a) 2.080 % (b) 20.800 % (c) 4.008 % (d) 40.800 %

148. The weight of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be **[CBSE-AIPMT 2014]**

(a) 5.4 g (b) 10.8 g (c) 54.0 g (d) 108.0 g

149. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 A of current is passed through molten Al_2O_3 for 6 h, what mass of aluminium is produced? (Assume 100% current efficiency, atomic mass of Al = 27 g mol^{-1}) **[CBSE-AIPMT 2009]**

(a) 9.0×10^3 g (b) 8.1×10^4 g
(c) 2.4×10^5 g (d) 1.3×10^4 g

150. A button cell used in watches functions as following.

$$Zn(s) + Ag_2O(s) + H_2O(l) \rightleftharpoons 2Ag(s) + Zn^{2+}(aq) + 2OH^-(aq)$$

If half-cell potentials are :

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s); E^\circ = -0.76 \text{ V}$$

$$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq); \quad E^\circ = 0.34 \text{ V}$$

The cell potential will be **[NEET 2013]**

(a) 1.10 V (b) 0.42 V (c) 0.84 V (d) 1.34 V

151. $E^\circ_{Fe^{2+}/Fe} = -0.441$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771$V the standard emf of the reaction

$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}$ will be **[CBSE-AIPMT 2006]**

(a) 0.111 V (b) 0.330 V (c) 1.653 V (d) 1.212 V

152. Consider the change in oxidation state of bromine corresponding to different emf values as shown in the diagram below.

$$BrO_4^- \xrightarrow{1.82 \text{ V}} BrO_3^- \xrightarrow{1.5 \text{ V}} HBrO \xrightarrow{1.595 \text{ V}} Br_2 \xrightarrow{1.0652 \text{ V}} Br^-$$

Then the species undergoing disproportionation is **[NEET 2018]**

(a) Br_2 (b) BrO_4^-
(c) BrO_3^- (d) HBrO

153. In the electrochemical cell Zn | $ZnSO_4$ (0.01 M) || $CuSO_4$(1.0M)| Cu, the emf of this Daniel cell is E_1. When the concentration $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to E_2. From the followings, which one is the relationship between E_1 and E_2? (Given, $\frac{RT}{F} = 0.059$) **[NEET 2017, 2003]**

(a) $E_1 = E_2$ (b) $E_1 < E_2$
(c) $E_1 > E_2$ (d) $E_2 = 0 \neq E_1$

154. The pressure of H_2 required to make the potential of H_2 electrode zero in pure water at 298 K is **[CBSE-AIPMT 2016, Phase I]**

(a) 10^{-12} atm (b) 10^{-10} atm (c) 10^{-4} atm (d) 10^{-14} atm

155. For the reduction of silver ions with copper metal, the standard cell potential was found to be + 0.46 V at 25°C. The value of standard Gibbs energy, ΔG° will be ($F = 96500$ C mol^{-1}) **[CBSE-AIPMT 2010]**

(a) – 89.0 kJ (b) – 89.0 J
(c) – 44.5 kJ (d) – 98.0 kJ

156. Standard free energies of formation (in kJ/mol) at 298 K are –237.2, –394.4 and –8.2 for $H_2O(l)$, d $CO_2(g)$ and pentane (g), respectively. The value of E°_{cell} for the pentane-oxygen fuel cell is **[CBSE-AIPMT 2008]**

(a) 1.968 V (b) 2.0968 V (c) 1.0968 V (d) 0.0968 V

157. The standard EMF of a galvanic cell involving cell reaction with $n = 2$ is found to be 0.295 V at 25° C. The equilibrium constant of the reaction would be (Given, $F = 96500$ C mol^{-1}, $R = 8.314$ JK^{-1} mol^{-1}) **[CBSE-AIPMT 2004]**

(a) 2.0×10^{11} (b) 4.0×10^{12} (c) 1.0×10^2 (d) 1.0×10^{10}

18. *Chemical Kinetics*

158. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, if $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol L^{-1}s^{-1}, the value of $\frac{-d[H_2]}{dt}$ would be **[CBSE-AIPMT 2009]**

(a) 3×10^{-4} mol L^{-1} s^{-1} (b) 4×10^{-4} mol L^{-1} s^{-1}
(c) 6×10^{-4} mol L^{-1} s^{-1} (d) 1×10^{-4} mol L^{-1} s^{-1}

159. Consider the reaction,

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is **[CBSE-AIPMT 2006]**

(a) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$ (b) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$
(c) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$ (d) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$

160. For the reaction, $A + B \longrightarrow$ products, it is observed that

I. On doubling the initial concentration of A only, the rate of reaction is also doubled and

II. On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is, given by **[CBSE-AIPMT 2009]**

(a) rate $= k[A]^2[B]$ (b) rate $= k[A][B]^2$
(c) rate $= k[A]^2[B]^2$ (d) rate $= k[A][B]$

161. Mechanism of a hypothetical reaction, $X_2 + Y_2 \longrightarrow 2XY$ is given below : **[NEET 2017]**

I. $X_2 \rightleftharpoons X + X$(fast)
II. $X + Y_2 \longrightarrow XY + Y$(slow)
III. $X + Y \longrightarrow XY$ (fast)

The overall order of the reaction will be

(a) 1 (b) 2 (c) 0 (d) 1.5

162. The rate of reaction between two reactants A and B decreases by a factor of 4, if the concentration of reactant B is doubled. The order of this reaction with respect to reactant B is **[CBSE-AIPMT 2005]**

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

163. A first order reaction has a specific reaction rate of 10^{-2}s^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g? **[NEET 2017]**

(a) 238.6 s (b) 138.6 s (c) 346.5 s (d) 693.0 s

164. For a first order reaction $A \longrightarrow B$, the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol $\text{L}^{-1}\text{s}^{-1}$. The half-life period of the reaction is **[CBSE-AIPMT 2005]**

(a) 220 s (b) 30 s (c) 300 s (d) 347 s

165. The correct difference between first-and second-order reactions is that

(a) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
(b) the half-life of a first-order reaction does not depend on $[A]_0$ the half-life of a second-order reaction does depend on $[A]_0$
(c) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
(d) the rate of a first-order reaction does depend on reactant concentrations; the rate of a second-order reaction does not depend on reactant concentrations

166. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction is ΔH (both of these in kJ/mol). Minimum value of E_a will be **[CBSE-AIPMT 2010]**

(a) less than ΔH (b) equal to ΔH
(c) more than ΔH (d) equal to zero

167. The activation energy of a reaction can be determined from the slope of which of the following graphs? **[CBSE-AIPMT 2015]**

(a) $\ln K$ vs T (b) $\frac{\ln K}{T}$ vs T (c) $\ln K$ vs $\frac{I}{T}$ (d) $\frac{T}{\ln K}$ vs $\frac{I}{T}$

168. The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{-2000/T}$ and $10^{15} \cdot e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is **[CBSE-AIPMT 2008]**

(a) 1000 K (b) $\frac{2000}{2.303}$ K (c) 2000 K (d) $\frac{1000}{2.303}$ K

169. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20° C to 35° C ? ($R = 8.314$ J mol^{-1} K^{-1}) **[NEET 2013]**

(a) 342 kJ mol^{-1} (b) 269 kJ mol^{-1}
(c) 34.7 kJ mol^{-1} (d) 15.1 kJ mol^{-1}

19. *Surface Chemistry*

170. Which of the following statements is correct for the spontaneous adsorption of a gas? **[CBSE-AIPMT 2014]**

(a) ΔS is negative and therefore, ΔH should be highly positive
(b) ΔS is negative and therefore, ΔH should be highly negative
(c) ΔS is positive and therefore, ΔH should be negative
(d) ΔS is positive and therefore, ΔH should also be highly positive

171. If x is amount of adsorbate and m is amount of adsorbent, which of the following relations is not related to adsorption process? **[CBSE-AIPMT 2011]**

(a) $\frac{x}{m} = f(T)$ at constant p (b) $p = f(T)$ at constant $\left(\frac{x}{m}\right)$
(c) $\frac{x}{m} = p \times T$ (d) $\frac{x}{m} = f(p)$ at constant T

172. For adsorption of a gas on a solid, the plot of $\log \frac{x}{m}$ vs $\log p$ is linear with slope equal to (n being a whole number) **[CBSE-AIPMT 2006, 1994]**

(a) k (b) $\log k$ (c) n (d) $\frac{1}{n}$

173. The Langmuir adsorption isotherm is deduced by using the assumption that **[CBSE-AIPMT 2007]**

(a) the adsorption takes place in multilayers
(b) the adsorption sites are equivalent in their ability to adsorb the particles
(c) the heat of adsorption varies with coverage
(d) the adsorbed molecules interact with each other

174. Which one of the following statements is incorrect about enzyme catalysis? **[CBSE-AIPMT 2012]**

(a) Enzymes are mostly proteinous in nature
(b) Enzyme action is specific
(c) Enzymes are denaturated by UV-rays and at high temperature
(d) Enzymes are least reactive at optimum temperature

175. Which property of colloidal solution is independent of charge on the colloidal particles? **[CBSE-AIPMT 2015, 2014]**

(a) Coagulation (b) Electrophoresis
(c) Electroosmosis (d) Tyndall effect

176. On which of the following properties does the coagulating power of an ion depend? **[NEET 2018]**

(a) Both magnitude and sign of the charge on the ion
(b) Size of the ion alone
(c) The magnitude of the charge on the ion alone
(d) The sign of charge on the ion alone

177. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given below :

I. (NaCl) = 52 II. ($BaCl_2$) = 0.69
III. ($MgSO_4$) = 0.22

The correct order of their coagulating power is **[NEET 2016, Phase II]**

(a) I > II > III (b) II > I > III (c) III > II > I (d) III > I > II

20. *General Principles and Process of Isolation of Elements*

178. Sulphide ores of metals are usually concentrated by froth floatation process. Which one of the following sulphide ores offers an exception and is concentrated by chemical leaching? **[CBSE-AIPMT 2007]**

(a) Argentite (b) Galena
(c) Copper pyrite (d) Sphalerite

179. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true? **[CBSE-AIPMT 2007]**

(a) Carbon and hydrogen are suitable reducing agents for metal sulphides
(b) The $\Delta_f G°$ of the sulphide is greater than those for CS_2 and H_2S
(c) The $\Delta_f G°$ is negative for roasting of sulphide ore to oxide
(d) Roasting of the sulphide to the oxide is thermodynamically feasible

180. Roasting of sulphides gives the gas X as a by-product. This is a colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic acts as a reducing agent and its acid has never been insolated. The gas X is **[NEET 2013]**

(a) H_2S (b) SO_2 (c) CO_2 (d) SO_3

181. Extraction of gold and silver involves leaching with CN^- ion. Silver is later recovered by **[NEET 2017]**

(a) liquation (b) distillation
(c) zone refining (d) displacement with Zn

182. Considering Ellingham diagram, which of the following metals can be used to reduce alumina? **[NEET 2018]**

(a) Mg (b) Zn (c) Fe (d) Cu

183. Aluminium is extracted from alumina (Al_2O_3) by electrolysis of a molten mixture of **[CBSE-AIPMT 2012]**

(a) $Al_2O_3 + HF + NaAlF_4$ (b) $Al_2O_3 + CaF_2 + NaAlF_4$
(c) $Al_2O_3 + Na_3AlF_6 + CaF_2$ (d) $Al_2O_3 + KF + Na_3AlF_6$

184. In the extraction of copper from its sulphide ore, the metal finally obtained by the reduction of cuprous oxide with **[CBSE-AIPMT 2015]**

(a) iron (II) sulphide (b) carbon monoxide
(c) copper (I) sulphide (d) sulphur dioxide

185. Match items of Column I with the items of Column II and assign the correct code. **[NEET 2016, Phase I]**

	Column I		Column II
A.	Cyanide process	1.	Ultrapure Ge
B.	Froth floatation process	2.	Dressing of ZnS
C.	Electrolytic reduction	3.	Extraction of Al
D.	Zone refining	4.	Extraction of Au
		5.	Purification of Ni

Codes

	A	B	C	D
(a)	2	3	1	5
(b)	1	2	3	4
(c)	3	4	5	1
(d)	4	2	3	1

21. *p-block Elements*

186. The correct order of N-compounds in its decreasing order of oxidation states is **[NEET 2018]**

(a) HNO_3, NH_4Cl, NO, N_2 (b) HNO_3, NO, NH_4Cl, N_2
(c) HNO_3, NO, N_2, NH_4Cl (d) NH_4Cl, N_2, NO, HNO_3

187. Which is the correct statement for the given acids? **[NEET 2016, Phase I]**

(a) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid
(b) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid
(c) Both are triprotic acids
(d) Both are diprotic acids

188. Strong reducing behaviour of H_3PO_2 is due to **[CBSE-AIPMT 2015]**

(a) presence of one —OH group and two P—H bonds
(b) high electron gain enthalpy of phosphorus
(c) high oxidation state of phosphorus
(d) presence of two —OH groups and one P—H bond

189. Which of the following statements is not valid for oxoacids of phosphorus? **[CBSE-AIPMT 2012]**

(a) Orthophosphoric acid is used in the manufacture of triple superphosphate
(b Hypophosphorus acid is a diprotic acid
(c) All oxoacids contain tetrahedral four coordinated phosphorus
(d) All oxoacids contain at least one P$=$O unit and one P—OH group

190. The formation of the oxide ion $O^{2-}(g)$, from oxygen atom requires first an exothermic and then an endothermic step as shown below :

$$O(g) + e^- \longrightarrow O^-(g);\ \Delta_f H^\circ = -141 \text{ kJ mol}^{-1}$$
$$O^-(g) + e^- \longrightarrow O^{2-}(g);\Delta_f H^\circ = +780 \text{ kJ mol}^{-1}$$

Thus, process of formation of O^{2-} in gas phase is unfavourable even though O^{2-} is isoelectronic with neon. It is due to the fact that **[CBSE-AIPMT 2015]**

(a) electron repulsion outweighs the stability gained by achieving noble gas configuration
(b) O^- ion has comparatively smaller size than oxygen atom
(c) oxygen is more electronegative
(d) addition of electron in oxygen result in large size of the ion

191. In which pair of ions both the species contain S—S bond? **[NEET 2017]**

(a) $S_2O_7^{2-}$, $S_2O_3^{2-}$ (b) $S_4O_6^{2-}$, $S_2O_3^{2-}$
(c) $S_2O_7^{2-}$, $S_2O_8^{2-}$ (d) $S_4O_6^{2-}$, $S_2O_7^{2-}$

192. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reaction does not show oxidising behaviour? **[NEET 2016, Phase II]**

(a) $Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
(b) $3S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$
(c) $C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$
(d) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

193. Which of the following statements is not true for halogens? **[NEET 2018]**

(a) All but fluorine show positive oxidation states
(b) All are oxidising agents
(c) All form monobasic oxyacids
(d) Chlorine has the highest electron-gain enthalpy

194. Which one of the following orders is not in accordance with the property stated against it? **[CBSE-AIPMT 2006]**

(a) $F_2 > Cl_2 > Br_2 > I_2$ (oxidising power)
(b) HI > HBr > HCl > HF (acidic property in water)
(c) $F_2 > Cl_2 > Br_2 > I_2$ (electronegativity)
(d) $F_2 > Cl_2 > Br_2 > I_2$ (bond dissociation energy)

195. The variation of the boiling point of the hydrogen halides is in the order HF > HI > HBr > HCl. What explains the higher boiling point of hydrogen fluoride? **[CBSE-AIPMT 2015]**

(a) The electronegativity of fluorine is much higher than for other elements in the group
(b) There is strong hydrogen bonding between HF molecules
(c) The bond energy of HF molecules is greater than in other hydrogen halides
(d) The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule

196. When Cl_2 gas reacts with hot and concentrated sodium hydroxide solution, the oxidation number of chlorine changes from **[CBSE-AIPMT 2012]**

(a) 0 to +1 and 0 to −5
(b) 0 to −1 and 0 to +5
(c) 0 to −1 and 0 to +3
(d) 0 to +1 and 0 to −3

197. Match the interhalogen compounds of Column I with the geometry in Column II and assign the correct code. **[NEET 2017]**

Column I		Column II
A.	XX'	1. T- shape
B.	XX'_3	2. Pentagonal bipyramidal
C.	XX'_5	3. Linear
D.	XX'_7	4. Square pyramidal
		5. Tetrahedral

Codes

	A	B	C	D
(a)	3	4	1	2
(b)	3	1	4	2
(c)	5	4	3	2
(d)	4	3	2	1

198. Among the following, which one is a wrong statement? **[NEET 2016, Phase II]**

(a) PH_5 and $BiCl_5$ do not exist
(b) $p\pi$-$d\pi$ bonds are present in SO_2
(c) SeF_4 and CH_4 have same shape
(d) I_3^+ has bent geometry

199. Match the compounds given in Column I with the hybridisation and shape given in Column II and mark the correct option. **[NEET 2016, Phase I]**

	Column I		Column II
A.	XeF_6	1.	Distorted octahedral
B.	XeO_3	2.	Square planar
C.	$XeOF_4$	3.	Pyramidal
D.	XeF_4	4.	Square pyramidal

Codes

	A	B	C	D
(a)	1	2	4	3
(b)	4	3	1	2
(c)	4	1	2	3
(d)	1	3	4	2

22. *d and f-block Elements*

200. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionisation enthalpy? **[CBSE-AIPMT 2005]**

(a) Vanadium ($Z = 23$) (b) Chromium ($Z = 24$)
(c) Iron ($Z = 26$) (d) Manganese ($Z = 25$)

201. Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code. **[NEET 2018]**

Column I	Column II
A. Co^{3+}	1. $\sqrt{8}$ BM
B. Cr^{3+}	2. $\sqrt{35}$ BM
C. Fe^{3+}	3. $\sqrt{3}$ BM
D. Ni^{2+}	4. $\sqrt{24}$ BM
	5. $\sqrt{15}$ BM

Codes

	A	B	C	D
(a)	4	1	2	3
(b)	1	2	3	4
(c)	4	5	2	1
(d)	3	5	1	2

202. Magnetic moment 2.84 BM is given by (At. no. Ni = 28, Ti = 22, Cr = 24, Co = 27) **CBSE-AIPMT 2015, 2014]**

(a) Ni^{2+} (b) Ti^{3+} (c) Cr^{3+} (d) Co^{2+}

203. The d-electron configurations of Cr^{2+}, Mn^{2+} Fe^{2+} and Co^{2+} are d^4, d^5, d^6 and d^7 respectively. Which one of the following will exhibit minimum paramagnetic behaviour? **[CBSE-AIPMT 2011]**

(At. no. $Cr = 24, Mn = 25, Fe = 26, Co = 27$)

(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Co(H_2O)_6]^{2+}$
(c) $[Cr(H_2O)_6]^{2+}$ (d) $[Mn(H_2O)_6]^{2+}$

204. Out of TiF_6^{2-}, CoF_6^{3-}, Cu_2Cl_2 and $NiCl_4^{2-}$ (at. no. Z of $Ti = 22, Co = 27, Cu = 29, Ni = 28$), the colourless species are **[CBSE-AIPMT 2009]**

(a) TiF_6^{2-} and CoF_6^{3-} (b) Cu_2Cl_2 and $NiCl_4^{2-}$
(c) TiF_6^{2-} and Cu_2Cl_2 (d) CoF_6^{3-} and $NiCl_4^{2-}$

205. $HgCl_2$ and I_2 both when dissolved in water containing I^- ions the pair of species formed is **[NEET 2017]**

(a) HgI_2, I_3^- (b) HgI_2, I^- (c) HgI_4^{2-}, I_3^- (d) Hg_2I_2, I^-

206. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution? **[NEET 2016, Phase I]**

(a) The solution is decolourised (b) SO_2 is reduced
(c) Green $Cr_2(SO_4)_3$ is formed (d) The solution turns blue

207. In acidic medium, H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two (—O—O—) bonds. Oxidation state of Cr in CrO_5 is **[CBSE-AIPMT 2014]**

(a) +5 (b) +3
(c) +6 (d) −10

208. Which one of the following ions exhibits d-d transition and paramagnetism as well? **[NEET 2018]**

(a) MnO_4^- (b) $Cr_2O_7^{2-}$ (c) CrO_4^{2-} (d) MnO_4^{2-}

209. The reaction of aqueous $KMnO_4$ with H_2O_2 in acidic conditions gives **[CBSE-AIPMT 2014]**

(a) Mn^{4+} and O_2 (b) Mn^{2+} and O_2
(c) Mn^{2+} and O_3 (d) Mn^{4+} and MnO_2

210. The electronic configurations of Eu (at. no. = 63), Gd (at. no. = 64) and Tb (at. no. = 65) are **[NEET 2016, Phase I]**

(a) [Xe] $4f^6 5d^1 6s^2$, [Xe] $4f^7 5d^1 6s^2$ and [Xe] $4f^9 6s^2$
(b) [Xe] $4f^6 5d^1 6s^2$, [Xe] $4f^7 5d^1 6s^2$ and [Xe] $4f^8 5d^1 6s^2$
(c) [Xe] $4f^7 6s^2$, [Xe] $4f^7 5d^1 6s^2$ and [Xe] $4f^9 6s^2$
(d) [Xe] $4f^7 6s^2$, [Xe] $4f^8 6s^2$ and [Xe] $4f^8 5d^1 6s^2$

211. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers). **[CBSE-AIPMT 2015]**

(a) Ti (22) and Zr (40)
(b) Zr (40) and Nb (41)
(c) Zr (40) and Hf (72)
(d) Zr (40) and Ta (73)

212. Identify the incorrect statement among the following. **[CBSE-AIPMT 2007]**

(a) There is a decrease in the radii of the atoms or ions as one proceeds from La or Lu
(b) Lanthanide contraction is the accumulation of successive shrinkages
(c) As a result of lanthanide contraction, the properties of 4 *d* series of the transition elements have no similarities with the 5 *d* series of elements
(d) Shielding power of 4*f* electrons is quite weak

213. Which of the following ions will exhibit colour in aqueous solutions? **[CBSE-AIPMT 2010]**

(a) La^{3+} ($Z = 57$) (b) Ti^{3+} ($Z = 22$)
(c) Lu^{3+} ($Z = 71$) (d) Sc^{3+} ($Z = 21$)

214. The reason for greater range of oxidation states in actinoids is attributed to **[NEET 2017]**

(a) the radioactive nature of actinoids
(b) actinoid contraction
(c) 5*f*, 6*d* and 7*s* levels having comparable energies
(d) 4*f* and 5*d* levels being close in energies

215. More number of oxidation states are exhibited by the actinides than by the lanthanides. The main reason for this is **[CBSE-AIPMT 2006, 2005]**

(a) more energy difference between 5*f* and 6*d*-orbitals than that between 4*f* and 5*d*-orbitals
(b) lesser energy difference between 5*f* and 6*d*-orbitals than that between 4*f* and 5*d*-orbitals
(c) greater metallic character of the lanthanides than that of the corresponding actinides
(d) more active nature of the actinides

23. *Coordination Compounds*

216. The correct order of the stoichiometrics of AgCl formed when $AgNO_3$ in excess is treated with the complexes $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5NH_3$, $CoCl_3 \cdot 4NH_3$ respectively is **[NEET 2017]**

(a) 1 AgCl, 3 AgCl, 2 AgCl (b) 3 AgCl, 1 AgCl, 2 AgCl
(c) 3 AgCl, 2 AgCl, 1 AgCl (d) 2 AgCl, 3 AgCl, 1 AgCl

217. The complex $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of which type of isomerism? **[CBSE-AIPMT 2011]**

(a) Ionisation isomerism (b) Coordination isomerism
(c) Geometrical isomerism (d) Linkage isomerism

218. The complex, $[Pt(Py)(NH_3)BrCl]$ will have how many geometrical isomers? **[CBSE-AIPMT 2011]**

(a) 4 (b) 0 (c) 2 (d) 3

219. Number of possible isomers for the complex $[Co(en)_2\ Cl_2]Cl$ will be (en = ethylenediamine) **[CBSE-AIPMT 2015]**

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

220. The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are **[NEET 2018]**

(a) square planar geometry and paramagnetic
(b) tetrahedral geometry and diamagnetic
(c) square planar geometry and diamagnetic
(d) tetrahedral geometry and paramagnetic

221. The hybridisation involved in complex $[Ni(CN)_4]^{2-}$ is (atomic number of Ni = 28) **[CBSE-AIPMT 2015]**

(a) dsp^2 (b) sp^3 (c) d^2sp^2 (d) d^2sp^3

222. Which of the following does not show optical isomerism? (en = ethylenediamine) **[CBSE-AIPMT 2009]**

(a) $[Co(en)_2Cl_2]^+$ (b) $[Co(NH_3)_3Cl_3]^0$
(c) $[Co(en)Cl_2(NH_3)_2]^+$ (d) $[Co(en)_3]^{3+}$

223. Which of the following will give a pair of enantiomers? (en = $NH_2CH_2CH_2NH_2$) **[CBSE-AIPMT 2007]**

(a) $[Cr(NH_3)_6][Co(CN)_6]$ (b) $[Co(en)_2Cl_2]Cl$
(c) $[Pt(NH_3)_4][PtCl_6]$ (d) $[Co(NH_3)_4Cl_2]NO_2$

224. Which of the following pairs of *d*-orbitals will have electron density along the axis? **[NEET 2016, Phase II]**

(a) d_{z^2}, d_{xz} (b) d_{xz}, d_{yz} (c) $d_{z^2}, d_{x^2-y^2}$ (d) $d_{xy}, d_{x^2-y^2}$

225. Which of the following coordination compounds would exhibit optical isomerism? **[CBSE-AIPMT 2004]**

(a) Pentaamminenitrocobalt (III) iodide
(b) Diamminedichloroplatinum (II)
(c) *trans*-dicyanobis (ethylenediamine) chromium (III) chloride
(d) *tris*-(ethylenediamine) cobalt (III) bromide

226. Which one of the following is an outer orbital complex and exhibits paramagnetic behaviour? **[CBSE-AIPMT 2012]**

(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Zn(NH_3)_6]^{2+}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Co(NH_3)_6]^{3+}$

227. Which of the following complexes exhibits the highest paramagnetic behaviour?
(where, gly = glycine, en = ethylenediamine and bpy = bipyridyl moities)
(At. no. of Ti = 22, V = 23, Fe = 26, Co = 27) **[CBSE-AIPMT 2008]**

(a) $[V(gly)_2(OH)_2(NH_3)_2]^+$ (b) $[Fe(en)(py)(NH_3)_2]^{2+}$
(c) $[Co(ox)_2(OH)_2]^-$ (d) $[Ti(NH_3)_6]^{3+}$

228. Which of the following complex ions is expected to absorb visible light?
(At. no. of Zn = 30, Sc = 21, Ti = 22 , Cr = 24) **[CBSE-AIPMT 2009]**

(a) $[Sc(H_2O)_3(NH_3)_3]^{3+}$ (b) $[Ti(en)_2(NH_3)_2]^{4+}$
(c) $[Cr(NH_3)_6]^{3+}$ (d) $[Zn(NH_3)_6]^{2+}$

229. $[Cr(H_2O)_6]Cl_3$ (at. no. of Cr = 24) has a magnetic moment of 3.83 BM, the correct distribution of 3*d* electrons in the chromium of the complex is **[CBSE-AIPMT 2006]**

(a) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{z^2}$ (b) $3d_{(x^2-y^2)}, 3d^1_{z^2}, 3d^1_{xz}$
(c) $3d_{xy}, 3d_{(x^2-y^2)}, 3d^1_{yz}$ (d) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}$

230. Among the following complexes, the one which shows zero crystal field stabilisation energy (CFSE) is **[CBSE-AIPMT 2014]**

(a) $[Mn(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{3+}$

231. Crystal field stabilisation energy for high spin d^4 octahedral complex is **[CBSE-AIPMT 2010]**

(a) $-1.8\Delta_o$ (b) $-1.6\Delta_o + p$
(c) $-1.2\,\Delta_o$ (d) $-0.6\Delta_o$

232. Correct increasing order for the wavelengths of absorption in the visible region for the complexes of CO^{3+} is **[NEET 2017]**

(a) $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$
(b) $[Co(H_2O)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$
(c) $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$
(d) $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(H_2O)_6]^{3+}$

233. Iron carbonyl, $Fe(CO)_5$ is **[NEET 2018]**

(a) trinuclear (b) mononuclear
(c) tetranuclear (d) dinuclear

234. Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 Å.) **[NEET 2016, Phase I]**

(a) $[Co(CO)_4]^-$ (b) $[Fe(CO)_4]^{2-}$
(c) $[Mn(CO)_6]^+$ (d) $Ni(CO)_4$

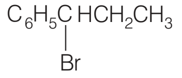
24. *Haloalkanes and Haloarenes*

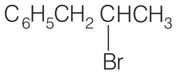
235. Which of the following reaction(s) can be used for the preparation of alkyl halides? **[CBSE-AIPMT 2015]**

I. $CH_3CH_2OH + HCl \xrightarrow{\text{Anhy. } ZnCl_2}$
II. $CH_3CH_2OH + HCl \longrightarrow$
III. $(CH_3)_3COH + HCl \longrightarrow$
IV. $(CH_3)_2CHOH + HCl \xrightarrow{\text{Anhy. } ZnCl_2}$

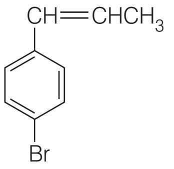
(a) I, III and IV (b) I and II
(c) Only IV (d) III and IV

236. The reaction of $C_6H_5CH{=}CHCH_3$ with HBr produces **[CBSE-AIPMT 2015]**

(a) 
$C_6H_5\underset{|\,Br}{C}HCH_2CH_3$

(b) 
$C_6H_5CH_2\underset{|\,Br}{C}HCH_3$

(c) $C_6H_5CH_2CH_2CH_2Br$

(d) 

237. Identity Z in the sequence of reactions, **[CBSE-AIPMT 2014]**

$$CH_3CH_2CH{=}CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

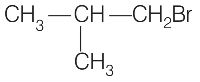
(a) $CH_3—(CH_2)_3—O—CH_2CH_3$
(b) $(CH_3)_2CH_2—O—CH_2CH_3$
(c) $CH_3(CH_2)_4—O—CH_3$
(d) $CH_3CH_2—CH(CH_3)—O—CH_2CH_3$

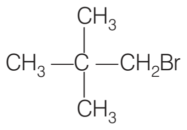
238. In a S_N2 substitution reaction of the type

$$R—Br + Cl^- \xrightarrow{DMF} R—Cl + Br^-.$$

Which one of the following has the highest relative rate? **[CBSE-AIPMT 2008]**

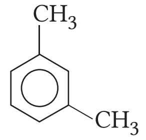
(a) $CH_3—CH_2—CH_2Br$

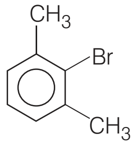
(b) 
$CH_3—\underset{|\,CH_3}{CH}—CH_2Br$

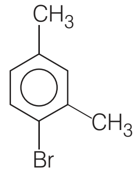
(c) 
$CH_3—\overset{CH_3\,|}{\underset{|\,CH_3}{C}}—CH_2Br$

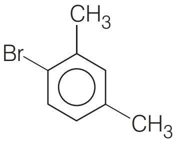
(d) CH_3CH_2Br

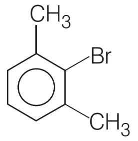
239. What products are formed when the following compound is treated with Br_2 in the presence of $FeBr_3$? **[CBSE-AIPMT 2014]**

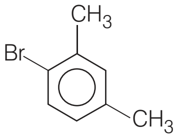


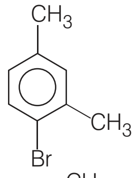
(a) 

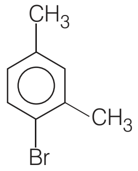
and 

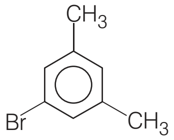
(b) 

and 

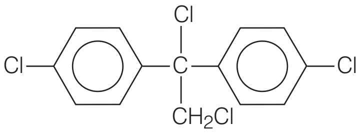
(c) 

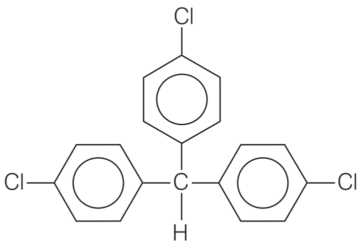
and 

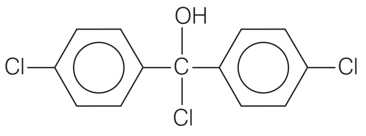
(d) 

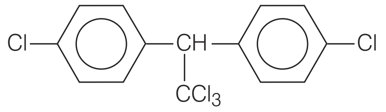
and 

240. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in the presence of sulphuric acid and produces. **[CBSE-AIPMT 2009]**

(a) 

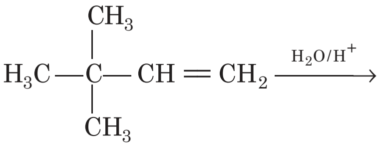
(b) 

(c) 

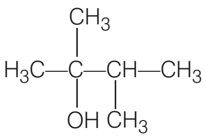
(d) 

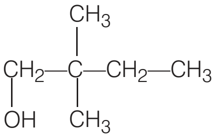
25. *Alcohols, Phenols and Ethers*

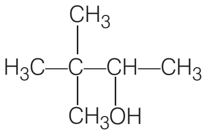
241. In the following reaction,

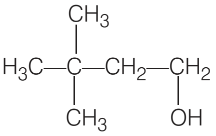

$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{H_2O/H^+}$

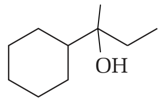
A + *B*
Major product Minor product **[CBSE-AIPMT 2012]**

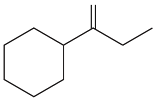
(a) 
$H_3C-\overset{CH_3}{\underset{OH}{C}}-\underset{CH_3}{CH}-CH_3$

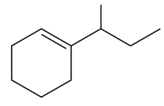
(b) 
$\underset{OH}{CH_2}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$

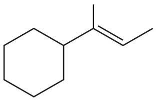
(c) 
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-CH_3$

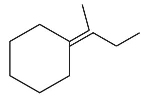
(d) 
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{OH}{CH_2}$

242. Which of the following is not the product of dehydration of  ? **[CBSE-AIPMT 2015]**

(a) 

(b) 

(c) 

(d) 

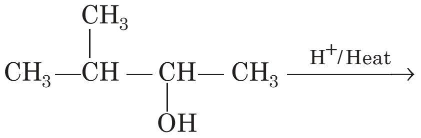
243. Consider the following reaction,

$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{Alc. KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4\text{, room temperature}} Z$$

The product *Z* is **[CBSE-AIPMT 2009]**

(a) $CH_2=CH_2$
(b) $CH_3CH_2OCH_2CH_3$
(c) $CH_3CH_2OSO_3H$
(d) CH_3CH_2OH

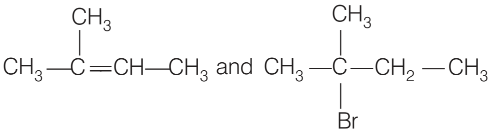
244. In the following reactions, **[CBSE-AIPMT 2011]**

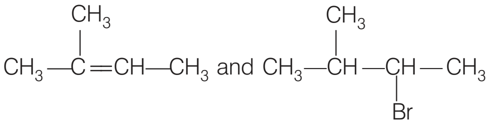
I. 
$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{H^+/\text{Heat}}$

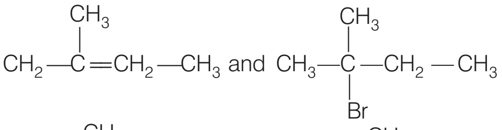
A + *B*
Major product Minor product

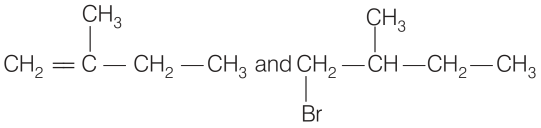
$$\text{II. } A \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\text{(Major product)}}{C} + \underset{\text{(Minor product)}}{D}$$

The major products *A* and *C* are respectively

(a) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

(b) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3$

(c) 
$CH_2-\overset{CH_3}{C}=CH_2-CH_3$ and $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

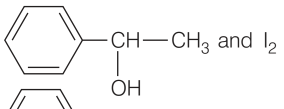
(d) 
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and $\underset{Br}{CH_2}-\overset{CH_3}{CH}-CH_2-CH_3$

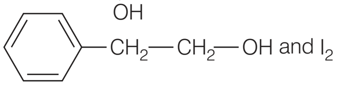
245. Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine? **[CBSE-AIPMT 2004]**

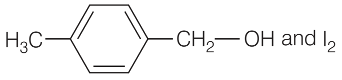
(a) $CH_3CH(OH)CH_3$
(b) $CH_3CH_2CH(OH)CH_3$
(c) CH_3OH
(d) CH_3CH_2OH

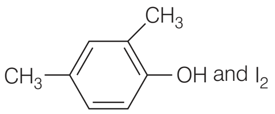
246. Compound *A*, $C_8H_{10}O$, is found to react with NaOI (produced by reacting *Y* with NaOH) and yields a yellow precipitate with characteristic smell.

A and *Y* are respectively **[NEET 2018]**

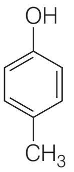
(a) 

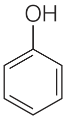
(b) 

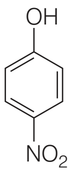
(c) 

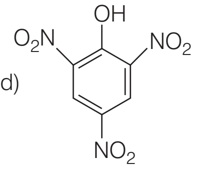
(d) 

247. Which one is the most acidic compound? **[NEET 2017]**

(a) 

(b) 

(c) 

(d) 

248. Given are cyclohexanol (I), acetic acid (II), 2, 4, 6-trinitrophenol (III) and phenol (IV). In these, the order of decreasing acidic character will be **[CBSE-AIPMT 2010]**

(a) III > II > IV > I
(b) II > III > I > IV
(c) II > III > IV > I
(d) III > IV > II > I

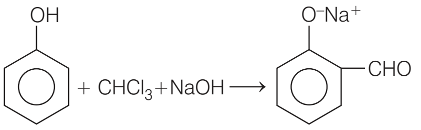
249. Consider the following reaction,

$$\text{Phenol} \xrightarrow{\text{Zn-dust}} X \xrightarrow[\text{Anhy. AlCl}_3]{\text{CH}_3\text{Cl}} Y \xrightarrow{\text{Alk. KMnO}_4} Z$$

The product Z is **[CBSE-AIPMT 2009]**

(a) toluene (b) benzaldehyde
(c) benzoic acid (d) benzene

250. In the reaction, **[NEET 2018]**

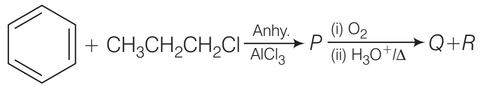


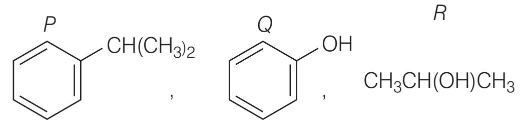
The electrophile involved is

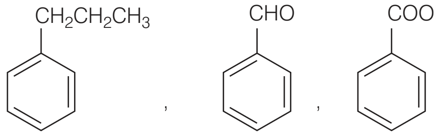
(a) dichloromethyl anion ($\bar{C}HCl_2$) (b) formyl cation ($\overset{+}{C}HO$)

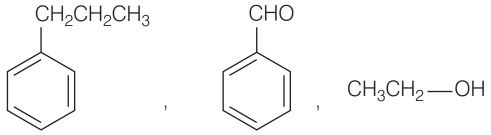
(c) dichloromethyl cation ($\overset{+}{C}HCl_2$) (d) dichlorocarbene ($:CCl_2$)

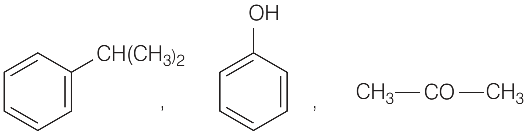
251. Identify the major products P, Q and R in the following sequence of reactions :



(a)


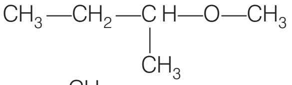
(b)


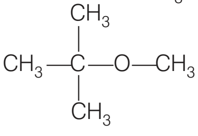
(c)


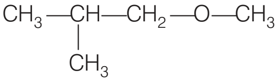
(d)


252. Among the following ethers which one will produce methyl alcohol on treatment with hot concentrated HI? **[CBSE-AIPMT 2013]**

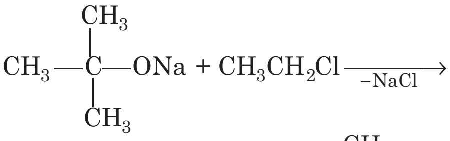
(a) $CH_3—CH_2—CH_2—CH_2—O—CH_3$

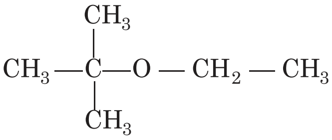
(b)

$CH_3—CH_2—\underset{\substack{|\\CH_3}}{C}H—O—CH_3$

(c)

$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—O—CH_3$

(d)

$CH_3—\underset{\substack{|\\CH_3}}{CH}—CH_2—O—CH_3$

253. The reaction,


$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—ONa + CH_3CH_2Cl \xrightarrow[-NaCl]{}$


$CH_3—\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}—O—CH_2—CH_3$

is called **[CBSE-AIPMT 2015]**

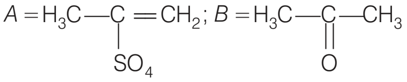
(a) Williamson synthesis
(b) Williamson continuous etherification process
(c) Etard reaction
(d) Gatterman-Koch reaction

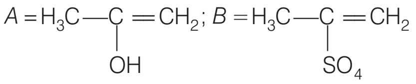
26. *Aldehyde, Ketone and Carboxylic Acid*

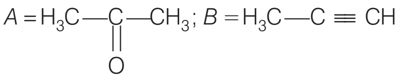
254. Predict the correct intermediate and product in the following reaction. **[NEET 2017]**

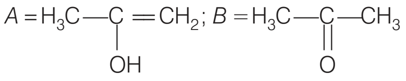
$$H_3C—C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ H_2SO_4}$$

Intermediate ⟶ Product
(A) (B)

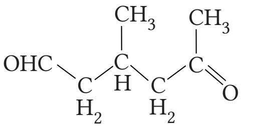
(a)

$A = H_3C—\underset{\substack{|\\SO_4}}{C}=CH_2$; $B = H_3C—\underset{\substack{||\\O}}{C}—CH_3$

(b)

$A = H_3C—\underset{\substack{|\\OH}}{C}=CH_2$; $B = H_3C—\underset{\substack{|\\SO_4}}{C}=CH_2$

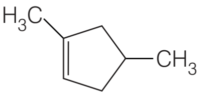
(c)

$A = H_3C—\underset{\substack{||\\O}}{C}—CH_3$; $B = H_3C—C\equiv CH$

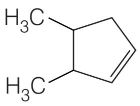
(d)

$A = H_3C—\underset{\substack{|\\OH}}{C}=CH_2$; $B = H_3C—\underset{\substack{||\\O}}{C}—CH_3$

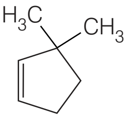
255. A single compound of the structure is

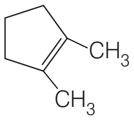


Obtainable from ozonolysis of which of the following cyclic compounds? **[CBSE-AIPMT 2015]**

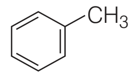
(a)


(b)


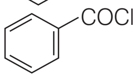
(c)


(d)


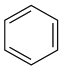
256. Reaction by which benzaldehyde cannot be prepared? **[NEET 2013]**

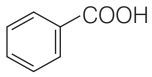
(a) 

+ CrO_2Cl_2 and CS_2 followed by H_3O^+

(b) 

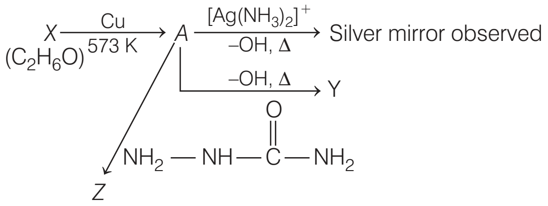
+ H_2 in presence of Pd-$BaSO_4$

(c)  + CO + HCl in presence of anhy. $AlCl_3$

(d) 

+ Zn/Hg and conc. HCl

257. Consider the reactions,



Identify A, X, Y and Z **[NEET 2017]**

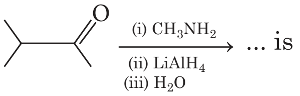
(a) *A*-methoxymethane, *X*-ethanoic acid, *Y*-acetate ion, *Z*-hydrazine

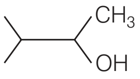
(b) *A*-methoxymethane, *X*-ethanol, *Y*-ethanoic acid, *Z*-semicarbazide

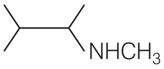
(c) *A*-ethanol, *X*-acetaldelyde, *Y*-but-2-enal, *Z*-semicarbazone

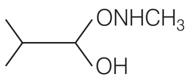
(d) *A*-ethanol, *X*-acetaldehyde, *Y*-butanone, *Z*-hydrazone

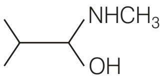
258. The major organic product formed from the following reaction **[CBSE-AIPMT 2005]**



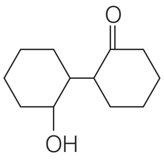
(a) 

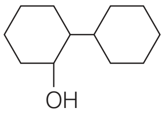
(b) 

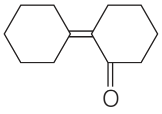
(c) 

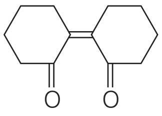
(d) 

259. Of the following which is the product formed when cyclohexanone undergoes aldol condensation followed by heating? **[NEET 2017]**

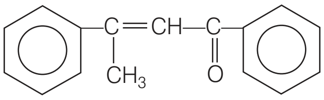
(a) 

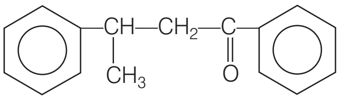
(b) 

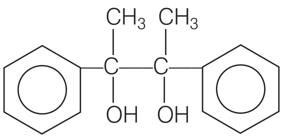
(c) 

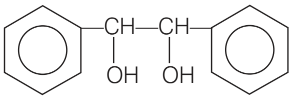
(d) 

260. Acetophenone when reacted with a base, C_2H_5ONa, yields a stable compound which has the structure. **[CBSE-AIPMT 2008]**

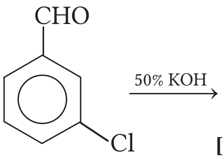
(a) 

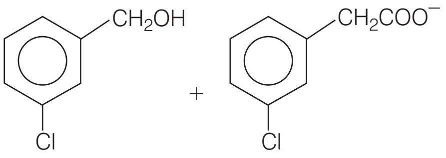
(b) 

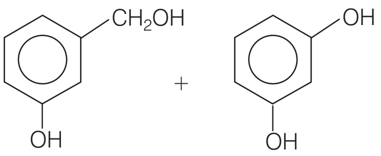
(c) 

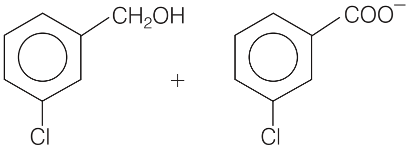
(d) 

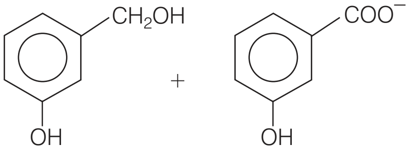
261. Predict the products in the given reaction, **[CBSE-AIPMT 2012]**



(a) 

(b) 

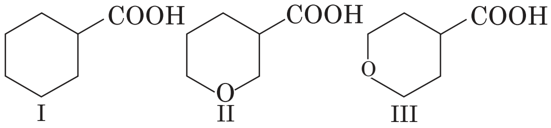
(c) 

(d) 

262. A carbonyl compound reacts with hydrogen cyanide to form cyanohydrin which on hydrolysis forms a racemic mixture of α-hydroxy acid. The carbonyl compound is **[CBSE AIPMT 2006]**

(a) acetaldehyde	(b) acetone
(c) diethyl ketone	(d) formaldehyde

263. The correct order of strengths of the carboxylic acids

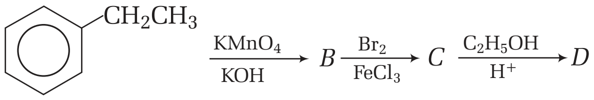


is

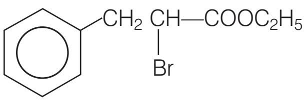
[NEET 2016, Phase II]

(a) I > II > III
(b) II > III > I
(c) III > II > I
(d) II > I > III

264. In a set of reactions, ethyl benzene yielded a product *D*. **[CBSE-AIPMT 2010]**



D would be

(a)


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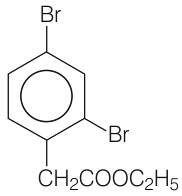

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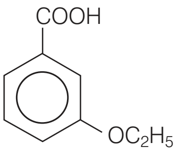

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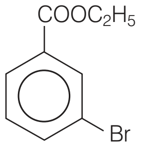
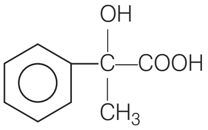
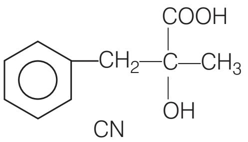


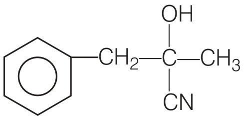
265. In a set of reactions, acetic acid yielded a product *D*.

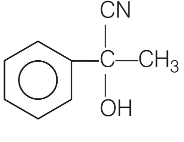
$$CH_3COOH \xrightarrow{SOCl_2} A \xrightarrow[\text{Anhy. } AlCl_3]{\text{Benzene}} B \xrightarrow{HCN} C \xrightarrow{HOH} D$$

The structure of *D* would be **[CBSE-AIPMT 2005]**

(a)


(b)


(c)


(d)


27. *Organic Compounds Containing Nitrogen*

266. Which of the following reactions is appropriate for converting acetamide to methanamine? **[NEET 2017]**

(a) Carbylamine reaction
(b) Hofmann Bromamide reaction
(c) Stephen's reaction
(d) Gabriel's phthalimide synthesis

267. Method by which aniline cannot be prepared is **[CBSE-AIPMT 2015]**

(a) hydrolysis phenyl isocyanide with acidic solution
(b) degradation of benzamide with bromine in alkaline solution
(c) reduction of nitrobenzene with H_2/Pd in ethanol
(d) potassium salt of phthalimide treated with chlorobenzene followed by the hydrolysis with aqueous NaOH solution

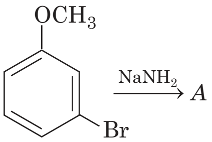
268. Acetamide is treated with the following reagents separately. Which one of these would yield methyl amine? **[CBSE-AIPMT 2010]**

(a) NaOH / Br_2
(b) Sodalime
(c) Hot conc. H_2SO_4
(d) PCl_5

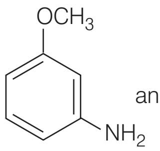
269. The correct statement regarding the basicity of arylamines is **[NEET 2016, Phase I]**

(a) arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π-electron system
(b) arylamines are generally more basic than alkylamines because of aryl group
(c) arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridised
(d) arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system.

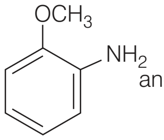
270. Identify *A* and predict the type of reactions



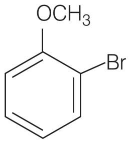
[NEET 2017]

(a)


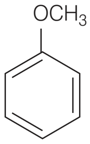
and substitution reaction

(b)


and elimination addition reaction

(c)


and cine substitution reaction

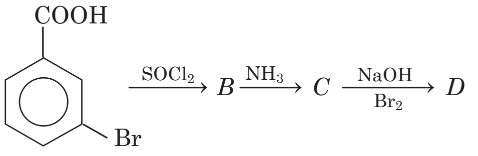
(d)


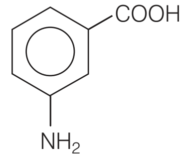
and cine substitution reaction

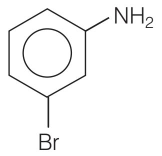
271. Nitration of aniline in strong acidic medium also gives *m*-nitroaniline because **[NEET 2018]**

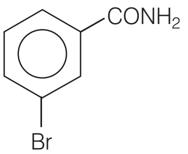
(a) in absence of substituents nitro group always goes to *m*-position
(b) in electrophilic substitution reactions amino group is *meta* directive
(c) in spite of substituents nitro group always goes to only *m*-position
(d) in acidic (strong) medium aniline is present as anilinium ion

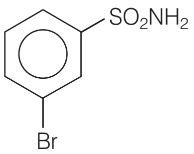
272. In a set of reactions, *m*-bromobenzoic acid gave a product *D*. Identify the product *D*. **[CBSE-AIPMT 2011]**



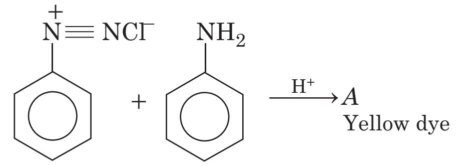
(a) 

(b) 

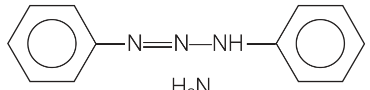
(c) 

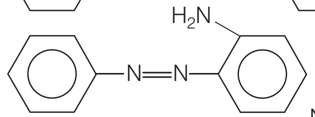
(d) 

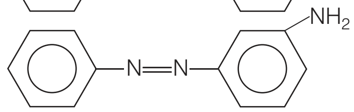
273. In the following reaction, the product (*A*) is

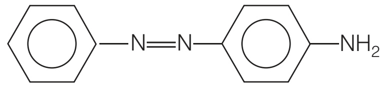


[CBSE-AIPMT 2014]

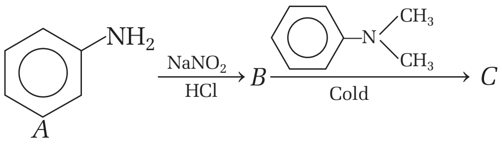
(a) 

(b) 

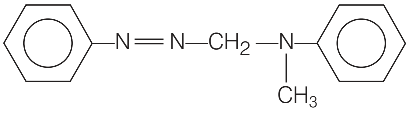
(c) 

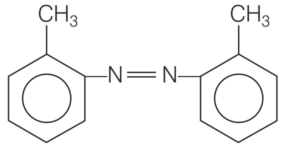
(d) 

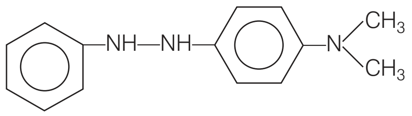
274. In a reaction of aniline a coloured products *C* was obtained.

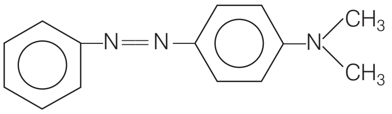


The structure of *C* would be **[CBSE-AIPMT 2008]**

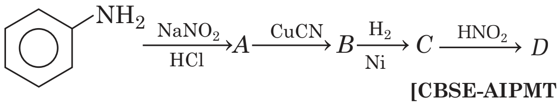
(a) 

(b) 

(c) 

(d) 

275. Aniline in a set of reactions yielded a product

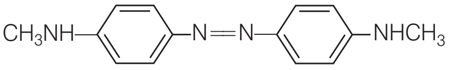


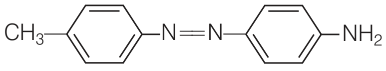
[CBSE-AIPMT 2005]

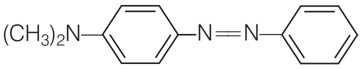
The structure of the product *D* would be

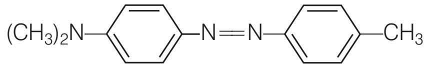
(a) $C_6H_5CH_2NH_2$
(b) $C_6H_5NHCH_2CH_3$
(c) C_6H_5NHOH
(d) $C_6H_5CH_2OH$

276. Aniline when diazotised in cold and then treated with dimethyl aniline, gives a coloured product. Its structure would be **[CBSE-AIPMT 2004]**

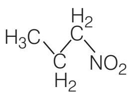
(a) 

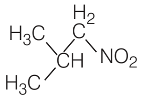
(b) 

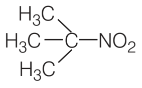
(c) 

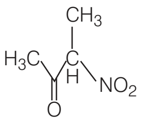
(d) 

277. Which one of the following nitro-compounds does not react with nitrous acid? **[NEET 2016, Phase II]**

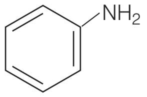
(a) 

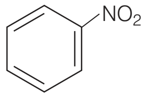
(b) 

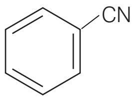
(c) 

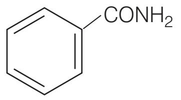
(d) 

278. A given nitrogen-containing aromatic compound *A* reacts with Sn/HCl, followed by HNO_2 to give an unstable compound *B*. *B*, on treatment with phenol, forms a beautiful coloured compound *C* with the molecular formula $C_{12}H_{10}N_2O$. The structure of compound *A* is **[NEET 2016, Phase II]**

(a) 

(b) 

(c) 

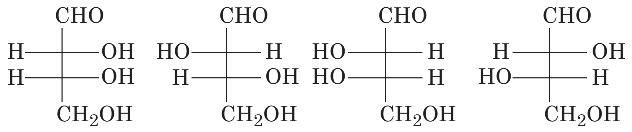
(d) 

28. *Biomolecules*

279. Which one given below is a non-reducing sugar? **[NEET 2016, Phase I]**

(a) Lactose (b) Glucose (c) Sucrose (d) Maltose

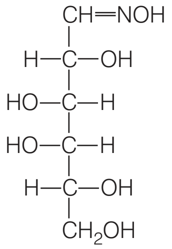
280. The correct corresponding order of names of four aldoses with configuration given below :

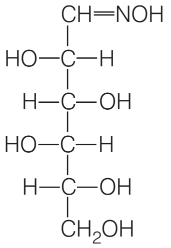


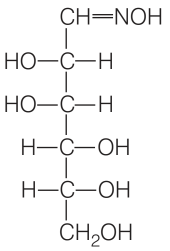
respectively, is **[NEET 2016, Phase II]**

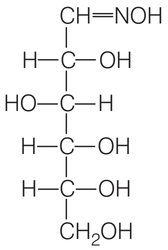
(a) L-erythrose, L-threose, L-erythrose, D-threose
(b) D-threose, D-erythrose, L-threose, L-erythrose
(c) L-erythrose, L-threose, D-erythrose, D-threose
(d) D-erythrose, D-threose, L-erythrose, L-threose

281. D-(+)-glucose reacts with hydroxyl amine and yields an oxime. The structure of the oxime would be **[CBSE-AIPMT 2014]**

(a) 

(b) 

(c) 

(d) 

282. Which one of the following statements is not true regarding (+)-lactose? **[CBSE-AIPMT 2011]**

(a) (+)-lactose is a β-glycoside formed by the union of a molecule of D-(+)-glucose and a molecule of D-(+)-galactose
(b) (+)-lactose is a reducing sugar and does not exhibit mutarotation
(c) (+)-lactose, $C_{12}H_{22}O_{11}$ contains 8 —OH groups
(d) On hydrolysis (+) lactose gives equal amount of D-(+)-glucose and D-(+)-galactose

283. Which of the following compounds can form a *Zwitter* ion?

(a) Benzoic acid (b) Acetanilide
(c) Aniline (d) Glycine

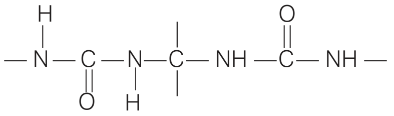
284. During the process of digestion, the proteins present in food materials are hydrolysed to amino acids. The two enzymes involved in the process

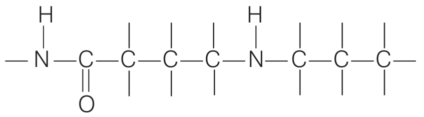
$$\text{Proteins} \xrightarrow{\text{Enzyme } (A)} \text{Polypeptides} \xrightarrow{\text{Enzyme } (B)} \text{Amino acids,}$$

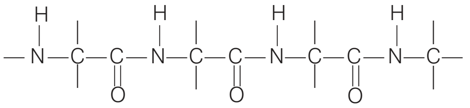
are respectively **[CBSE-AIPMT 2006]**

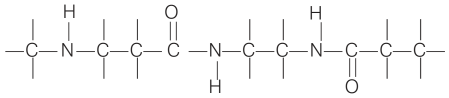
(a) amylase and maltase
(b) diastase and lipase
(c) pepsin and trypsin
(d) invertase and zymase

285. Which one of the following structures represents the peptide chain? **[CBSE AIPMT 2004]**

(a) 

(b) 

(c) 

(d) 

286. Which of the following statements is not correct? **[NEET 2017]**

(a) Insulin maintains sugar level in the blood of a human body
(b) Ovalbumin is a simple food reserve in egg white
(c) Blood proteins thrombin and fibrinogen are involved in blood clotting
(d) Denaturation makes the proteins more active

287. The correct statement regarding RNA and DNA, respectively is **[NEET 2016, Phase I]**

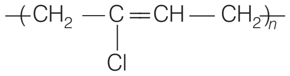
(a) the sugar component in RNA is ribose and the sugar component in DNA is 2′-deoxyribose
(b) the sugar component in RNA is arabinose and the sugar component in DNA is ribose
(c) the sugar component in RNA is 2′-deoxyribose and the sugar component in DNA is arabinose
(d) the sugar component in RNA is arabinose and the sugar component in DNA is 2′-deoxyribose

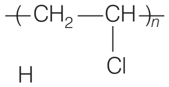
29. *Polymers*

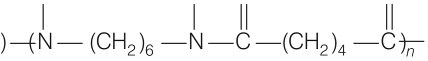
288. Regarding cross-linked or network polymers, which of the following statements is incorrect? **[NEET 2018]**

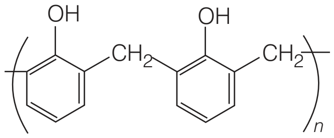
(a) Examples are bakelite and melamine
(b) They are formed from bi- and tri-functional monomers
(c) They contain covalent bonds between various linear polymer chains
(d) They contain strong covalent bonds in their polymer chains

289. Which one of the following is an example of a thermosetting polymer? **[CBSE-AIPMT 2014]**

(a) 
$(CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2)_n$

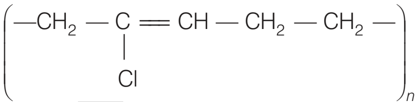
(b) 
$(CH_2-\underset{Cl}{\underset{|}{CH}})_n$

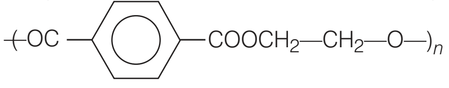
(c) 
$(\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}})_n$

(d) 

290. Structures of some common polymers are given. Which one is not correctly presented? **[CBSE-AIPMT 2009]**

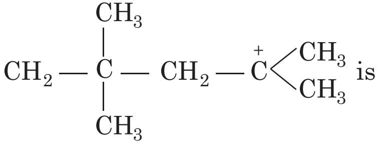
(a) Teflon $(CF_2-CF_2-)_n$

(b) Neoprene 
$\left(-CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2-CH_2-\right)_n$

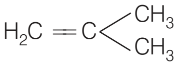
(c) Terylene 

(d) Nylon-6,6 $[NH(CH_2)_6NHCO(CH_2)_4-CO-]_n$

291. The monomer of the polymer


$CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{+}{C}{<}^{CH_3}_{CH_3}$ is

[CBSE-AIPMT 2005]

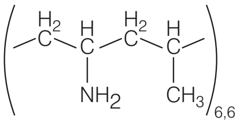
(a) 
$H_2C=C{<}^{CH_3}_{CH_3}$

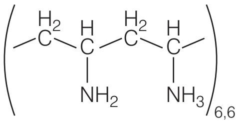
(b) $(CH_3)_2C=C(CH_3)_2$

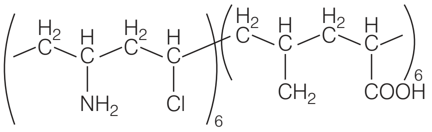
(c) $CH_3CH=CH\cdot CH_3$

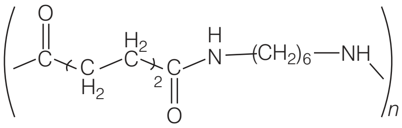
(d) $CH_3CH=CH_2$

292. Which one of the following structures represents nylon-6,6 polymer? **[NEET 2016, Phase II]**

(a) 

(b) 

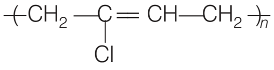
(c) 

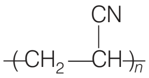
(d) 

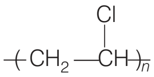
293. Which of the following organic compounds polymerises to form the polyester dacron? **[CBSE-AIPMT 2014]**

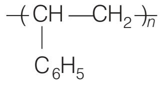
(a) Propylene and *para* —HO —(C_6H_4)— OH
(b) Benzoic acid and ethanol
(c) Terephthalic acid and ethylene glycol
(d) Benzoic acid and *para* —HO — (C_6H_4)— OH

294. Which of the following structures represents neoprene polymer? **[CBSE-AIPMT 2010]**

(a) 
$(CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2)_n$

(b) 
$(CH_2-\overset{CN}{\overset{|}{CH}})_n$

(c) 
$(CH_2-\overset{Cl}{\overset{|}{CH}})_n$

(d) 
$(\underset{C_6H_5}{\underset{|}{CH}}-CH_2)_n$

30. *Chemistry in Everyday Life*

295. Which one of the following is employed as a tranquilizer drug ? **[CBSE-AIPMT 2010]**

(a) Promethazine
(b) Valium
(c) Naproxen
(d) Mifepristone

296. Which one of the following is employed as antihistamine? **[CBSE-AIPMT 2011]**
(a) Diphenyl hydramine (b) Norethindrone
(c) Omeprazole (d) Chloramphenicol

297. Which of the following is an analgesic? **[NEET 2016, Phase I]**
(a) Penicillin (b) Streptomycin (c) Chloromycetin (d) Novalgin

298. Antiseptics and disinfectants either kill or prevent growth of microorganisms. Identify which of the following is not true. **[NEET 2013]**
(a) A 0.2% solution of phenol is an antiseptic while 1% solution acts as a disinfectant
(b) Chlorine and iodine are used as strong disinfectants
(c) Dilute solutions of boric acid and hydrogen, peroxide are strong antiseptics
(d) Disinfectants harm the living tissues

299. Artificial sweetener which is stable under cold conditions only is **[CBSE-AIPMT 2014]**
(a) saccharine (b) sucralose
(c) aspartame (d) alitame

Answer Sheet

1. *(d)*	2. *(b)*	3. *(c)*	4. *(b)*	5. *(a)*	6. *(d)*	7. *(a)*	8. *(b)*	9. *(c)*	10. *(c)*
11. *(c)*	12. *(d)*	13. *(c)*	14. *(a)*	15. *(a)*	16. *(c)*	17. *(d)*	18. *(c)*	19. *(a)*	20. *(c)*
21. *(d)*	22. *(a)*	23. *(a)*	24. *(d)*	25. *(d)*	26. *(c)*	27. *(a)*	28. *(b)*	29. *(*)*	30. *(b)*
31. *(a)*	32. *(a)*	33. *(b)*	34. *(b)*	35. *(b)*	36. *(c)*	37. *(c)*	38. *(d)*	39. *(d)*	40. *(b)*
41. *(d)*	42. *(b)*	43. *(b)*	44. *(b)*	45. *(d)*	46. *(a)*	47. *(c)*	48. *(d)*	49. *(d)*	50. *(*)*
51. *(c)*	52. *(d)*	53. *(c)*	54. *(b)*	55. *(a)*	56. *(a)*	57. *(a)*	58. *(b)*	59. *(b)*	60. *(b, d)*
61. *(c)*	62. *(c)*	63. *(b)*	64. *(c)*	65. *(b)*	66. *(c)*	67. *(b)*	68. *(d)*	69. *(b)*	70. *(c)*
71. *(d)*	72. *(a)*	73. *(c)*	74. *(b)*	75. *(b)*	76. *(c)*	77. *(b)*	78. *(d)*	79. *(c)*	80. *(c, d)*
81. *(b)*	82. *(b)*	83. *(d)*	84. *(c)*	85. *(c)*	86. *(b)*	87. *(a)*	88. *(b)*	89. *(d)*	90. *(b)*
91. *(d)*	92. *(b)*	93. *(c)*	94. *(b)*	95. *(c)*	96. *(a)*	97. *(b)*	98. *(d)*	99. *(a)*	100. *(a)*

101. *(c)*	102. *(b)*	103. *(a)*	104. *(c)*	105. *(d)*	106. *(d)*	107. *(c)*	108. *(a)*	109 *(c)*	110. *(d)*
111. *(a)*	112. *(c)*	113. *(d)*	114. *(b)*	115. *(b)*	116. *(d)*	117. *(d)*	118. *(d)*	119 *(c)*	120. *(b)*
121. *(d)*	122. *(b)*	123. *(d)*	124. *(c)*	125. *(a)*	126. *(b)*	127. *(a)*	128. *(a)*	129. *(a)*	130. *(d)*
131. *(a, d)*	132. *(c)*	133. *(d)*	134. *(d)*	135. *(a)*	136. *(d)*	137. *(d)*	138. *(d)*	139. *(a)*	140. *(d)*
141. *(a)*	142. *(a)*	143. *(a)*	144. *(b)*	145. *(d)*	146. *(b)*	147. *(c)*	148. *(d)*	149. *(b)*	150. *(a)*
151. *(d)*	152. *(d)*	153. *(c)*	154. *(d)*	155. *(a)*	156. *(c)*	157. *(d)*	158. *(a)*	159. *(b)*	160. *(b)*
161. *(d)*	162. *(b)*	163. *(b)*	164. *(d)*	165. *(b)*	166. *(c)*	167. *(c)*	168. *(d)*	169. *(c)*	170. *(b)*
171. *(c)*	172. *(d)*	173. *(b)*	174. *(d)*	175. *(d)*	176. *(a)*	177. *(c)*	178. *(d)*	179. *(a)*	180. *(b)*
181. *(d)*	182. *(a)*	183. *(c)*	184. *(c)*	185. *(d)*	186. *(c)*	187. *(a)*	188. *(a)*	189. *(b)*	190. *(a)*
191. *(b)*	192. *(d)*	193. *(a)*	194. *(d)*	195. *(b, c)*	196. *(b)*	197. *(b)*	198. *(c)*	199. *(d)*	200. *(d)*

201. *(c)*	202. *(a)*	203. *(b)*	204. *(c)*	205. *(c)*	206. *(c)*	207. *(c)*	208. *(d)*	209. *(b)*	210. *(c)*
211. *(c)*	212. *(c)*	213. *(b)*	214. *(c)*	215. *(b)*	216. *(c)*	217. *(b)*	218. *(d)*	219. *(c)*	220. *(b)*
221. *(a)*	222. *(b)*	223. *(b)*	224. *(c)*	225. *(d)*	226. *(a, b)*	227. *(c)*	228. *(c)*	229. *(d)*	230. *(b)*
231. *(d)*	232. *(a)*	233. *(b)*	234. *(b)*	235. *(a)*	236. *(a)*	237. *(a)*	238. *(d)*	239. *(c)*	240. *(d)*
241. *(a)*	242. *(b)*	243. *(d)*	244. *(a)*	245. *(c)*	246. *(a)*	247. *(d)*	248. *(a)*	249. *(c)*	250. *(d)*
251. *(d)*	252. *(c)*	253. *(a)*	254. *(d)*	255. *(a)*	256. *(d)*	257. *(c)*	258. *(b)*	259. *(c)*	260. *(a)*
261. *(c)*	262. *(a)*	263. *(b)*	264. *(d)*	265. *(a)*	266. *(b)*	267. *(d)*	268. *(a)*	269. *(d)*	270. *(a)*
271. *(d)*	272. *(b)*	273. *(d)*	274. *(d)*	275. *(d)*	276. *(c)*	277. *(c)*	278. *(b)*	279. *(c)*	280. *(d)*
281. *(d)*	282. *(b)*	283. *(d)*	284. *(c)*	285. *(c)*	286. *(d)*	287. *(a)*	288. *(d)*	289. *(d)*	290. *(b)*
291. *(a)*	292. *(d)*	293. *(c)*	294. *(a)*	295. *(b)*	296. *(a)*	297. *(d)*	298. *(c)*	299. *(c)*	

SOLUTIONS

1. *Some Basic Principles of Chemistry*

1. Average atomic mass

$$= \bar{A} = \frac{A_1X_1 + A_2X_2 + A_3X_3}{X_1 + X_2 + X_3}$$

where, $A_1A_2A_3$ = atomic mass

$X_1X_2X_3$ = percentage

$$= \frac{200 \times 90 + 199 \times 8.0 + 202 \times 2.0}{100}$$

$$= 199.96 \approx 200\,\text{u}$$

2. If Avogadro number N_A, is changed from $6.022 \times 10^{23}\,\text{mol}^{-1}$ to $6.022 \times 10^{20}\,\text{mol}^{-1}$, this would change the mass of one mole of carbon.

$\because$ 1 mole of carbon has mass = 12 g

or 6.022×10^{23} atoms of carbon have mass = 12 g

$\therefore 6.022 \times 10^{20}$ atoms of carbon have mass

$$= \frac{12}{6.022 \times 10^{23}} \times 6.022 \times 10^{20}$$

$$= 0.012\ \text{g}$$

3. Number of molecules = Mole × Avogadro's number (N_A)

The number of molecules of water in each of the given options is calculated as :

(a) 0.00224 L of water vapours at 1 atm and 273 K. At STP [1 atm and 273 K],

Number of moles [with reference to volume]

$$= \frac{\text{Volume of gas in litres}}{22.4}$$

$$= \frac{0.00224}{22.4}$$

$$= 0.0001$$

Number of molecules of water

$$= 0.0001 \times N_A$$

(b) 0.18 g of water

$$n_{H_2O} = \frac{m_{H_2O}}{M_{H_2O}}$$

$$= \frac{0.18}{18} = 0.01$$

Number of molecules of water

$$= 0.01 \times N_A$$

(c) 18 mL of water

Number of moles (n_{H_2O})

$$= \frac{\text{Mass of substance in g } (m_{H_2O})}{\text{Molar mass in g mol}^{-1}\ (M_{H_2O})}$$

m_{H_2O} = 18 g

[$\because$ Density of water (d_{H_2O}) = 1 g L^{-1}]

$$\therefore\ n_{H_2O} = \frac{18}{18} = 1$$

Number of molecules of water

$$= 1 \times N_A$$

(d) 10^{-3} moles of water

Number of molecules of water

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

$\therefore$ Among the given options. Option (c) contains the maximum number of water molecules.

4. Number of atoms = number of moles $\times N_A$ × atomicity

$$= 0.1 \times 6.023 \times 10^{23} \times 3$$

$$= 1.806 \times 10^{23}\ \text{atoms}$$

5. Given, molarity of solution = 2

Volume of solution = 250 mL

$$= \frac{250}{1000} = \frac{1}{4}\ \text{L}$$

Molar mass of HNO_3

$$= 1 + 14 + 3 \times 16$$

$$= 63\ \text{g mol}^{-1}$$

$\because$ Molarity

$$= \frac{\text{weight of } HNO_3}{\text{molecular mass of } HNO_3 \times \text{volume of solution (L)}}$$

$\therefore$ Weight of HNO_3

= molarity × molecular mass × volume (L)

$$= 2 \times 63 \times \frac{1}{4} = 31.5\ \text{g}$$

It is the weight of 100% HNO_3, but the given acid is 70% HNO_3.

$$\therefore\ \text{Its weight} = 31.5 \times \frac{100}{70}\ \text{g}$$

$$= 45\ \text{g}$$

6. In the given problem we have provided practical yield of MgO. For calculation of percentage yield of MgO, we need theoretical yield of MgO. For this we shall use mole concept.

$$MgCO_3(s) \longrightarrow MgO(s) + CO_2(g) \quad \ldots\text{(i)}$$

$$\text{Moles of } MgCO_3 = \frac{\text{Mass of substance in gram}}{\text{Molecular mass}}$$

$$= \frac{20}{84} = 0.238\ \text{mol}$$

From Eq. (i)

1 mole of $MgCO_3$ gives

= 1 mol MgO

$\therefore$ 0.238 mol $MgCO_3$ will give

= 0.238 mol MgO

= 0.238 × 40 g

= 9.52 g MgO

Now, practical yield of MgO = 8 g

$$\therefore\ \%\ \text{purity} = \frac{8}{9.52} \times 100$$

$$= 84\%$$

Alternate Method

$$\underset{84\ \text{g}}{MgCO_3} \longrightarrow \underset{40\ \text{g}}{MgO} + CO_2$$

$\therefore$ 8 g MgO will be form from $\frac{84}{5}$ g of $MgCO_3$.

$$\therefore\ \%\ \text{purity} = \frac{84}{5} \times \frac{100}{20}$$

$$= 84\%$$

7. Firstly, write the reaction of formic acid and oxalic acid with conc. H_2SO_4, respectively. Then, find the gaseous products formed and identify the remaining gaseous product after passing through KOH. Finally, calculate the total number of moles of gaseous product.

$$\begin{array}{lccc} & \underset{\text{Formic acid}}{HCOOH} \xrightarrow[\text{Dehydrating agent}]{\text{Conc.}H_2SO_4} & CO(g) + & H_2O(l) \\ \text{Initial moles} & \frac{2.3}{46} = \frac{1}{20}\ \text{mol} & 0 & 0 \\ \text{Final moles} & 0 & \frac{1}{20} & \frac{1}{20} \end{array}$$

Similarly,

$$\begin{array}{lcccc} & \underset{\text{Oxalic acid}}{\begin{array}{c}COOH\\ |\\ COOH\end{array}} \xrightarrow{\text{Conc.}H_2SO_4} & CO(g) + & CO_2(g) + & H_2O(l) \\ \text{Initial moles} & \frac{4.5}{90} = \frac{1}{20}\ \text{mol} & 0 & 0 & 0 \\ \text{Final moles} & 0 & \frac{1}{20} & \frac{1}{20} & \frac{1}{20} \end{array}$$

Now, $H_2O(l)$ gets absorbed by conc. H_2SO_4 in both reactions. Gaseous mixture CO and CO_2 when passed through KOH, only CO_2 gets absorbed. Thus, CO is the remaining gas.

Total number of moles of CO formed in above both equations

$$= \frac{1}{20} + \frac{1}{20} = \frac{1}{10}$$

$\because \quad \text{Moles} = \dfrac{\text{Given mass}}{\text{Molar mass}}$

$\therefore$ Weight of CO formed

$$= \frac{1}{10} \times 28 = 2.8 \text{ g}$$

Thus, weight of the remaining product at STP will be 2.8 g.

8. In acidic medium MnO_4^- oxidises ferrous oxalate as follows :

$$2\,MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$\because$ 5 moles of ferrous oxalate ions are oxidised by 2 moles of MnO_4^-.

$\therefore$ 1 mole of ferrous oxalate ion is oxidised by

$$= \frac{2}{5} \text{ moles of } MnO_4^-$$

$$= 0.4 \text{ mole of } MnO_4^-$$

9. In alkaline medium, $KMnO_4$ is reduced to K_2MnO_4

$$KI + H_2O \longrightarrow KOH + HI$$

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Hence, one mole of $KMnO_4$ is reduced by one mole of KI.

10. For the calculation of mass of AgCl precipitated, we find mass of $AgNO_3$ and NaCl in equal volume with the help of mole concept.

16.9% solution of $AgNO_3$ means 16.9 g $AgNO_3$ is present in 100 mL solution.

$\therefore$ 8.45 g $AgNO_3$ will be present in 50 mL solution.

Similarly, 5.8 g NaCl is present in 100 mL solution

$\therefore$ 2.9 g NaCl is present in 50 mL solution

	$AgNO_3$ +	NaCl $\longrightarrow$	AgCl +	$NaNO_3$
Initial mole	$\dfrac{8.45}{169.8}$	$\dfrac{2.9}{58.5}$	0	0
	= 0.049	= 0.049		
After reaction	0	0	0.049	0.049

$\therefore$ Mass of AgCl precipitated

$$= 0.049 \times 143.5$$

$$= 7 \text{ g}$$

11. $$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

	H_2	$\frac{1}{2}O_2$	H_2O
General reaction	1 mol	$\frac{1}{2}$ mol	1 mol
Initial reaction	$\frac{10}{2}$ mol	$\frac{64}{32}$ mol	?
	5 mol	2 mol	?

$\because \frac{1}{2}$ mole of O_2 gives

$$= 1 \text{ mole of } H_2O$$

$\therefore$ 2 moles of O_2 will give

$$= 1 \times 2 \times 2$$

$$= 4 \text{ moles of water}$$

12.

PbO +	$2HCl$ $\longrightarrow$	$PbCl_2 + H_2O$
207 + 16 = 223 (1 mol)	2 × 36.5 = 73 (2 mol)	(1 mol)

$$\text{Mole of PbO} = \frac{6.5}{223} = 0.029$$

$$\text{Mole of HCl} = \frac{3.2}{36.5} = 0.087$$

Since, 1 mole of PbO reacts with 2 moles of HCl, thus in this reaction PbO is the limiting reagent.

Hence, 1 mole of PbO forms

$$= 1 \text{ mole of } PbCl_2$$

0.029 mole of PbO will form

$$= 0.029 \text{ mole of } PbCl_2$$

13.

C_3H_8 +	$5O_2$ $\longrightarrow$	$3CO_2 + 4H_2O$
1 × 22.4 L	5 × 22.4 L	

For the combustion of 22.4 L propane, oxygen required

$$= 5 \times 22.4 \text{ L}$$

For the combustion of 1 L of propane, oxygen required

$$= \frac{5 \times 22.4}{22.4} \text{ L} = 5 \text{ L}$$

14. The given problem is related to the concept of stoichiometry of chemical equations. Thus, we have to convert the given volumes into their moles and then, identify the limiting reagent [possessing minimum number of moles and gets completely used up in the reaction]. The limiting reagent gives the moles of product formed in the reaction.

	$H_2(g) +$	$Cl_2(g) \longrightarrow$	$2HCl\,(g)$
Initial vol.	22.4 L	11.2 L	2 mol

$\because$ 22.4 L volume at STP is occupied by Cl_2 = 1 mol

$\therefore$ 11.2 L volume will be occupied by

$$Cl_2 = \frac{1 \times 11.2}{22.4} \text{ mol} = 0.5 \text{ mol}$$

22.4 L volume at STP is occupied by H_2 = 1 mol

Thus, $H_2(g) + Cl_2(g) \longrightarrow 2HCl\,(g)$

1 mol 0.5 mol

Since, Cl_2 possesses minimum number of moles, thus it is the limiting reagent.

As per equation,

1 mole of Cl_2 = 2 moles of HCl

$\therefore$ 0.5 mole of Cl_2

$$= 2 \times 0.5 \text{ mole of HCl}$$

$$= 1.0 \text{ mole of HCl}$$

Hence, 1.0 mole of HCl (*g*) is produced by 0.5 mole of Cl_2 [or 11.2 L].

15. The balanced chemical equation is

Mg +	$\frac{1}{2}O_2 \longrightarrow$	MgO
24 g	16 g	40 g

From the above equation, it is clear that, 24 g of Mg reacts with 16 g of O_2.

Thus, 1.0 g of Mg reacts with $\dfrac{16}{24}$ g of O_2 or 0.67 g of O_2.

But only 0.56 g of O_2 is available which is less than 0.67 g. Thus, O_2 is the limiting reagent.

Further, 16 g of O_2 reacts with 24 g of Mg.

$\therefore$ 0.56 g of O_2 will react with Mg

$$= \frac{24}{16} \times 0.56 = 0.84 \text{ g}$$

$\therefore$ Amount of Mg left unreacted

$$= (1.0 - 0.84) \text{ g Mg} = 0.16 \text{ g Mg}$$

2. *Structure of Atoms*

16. Ionisation energy of H

$$= 2.18 \times 10^{-18} \text{ J atom}^{-1}$$

$$E_n = \frac{-2.18 \times 10^{-18}}{n^2} \text{ J atom}^{-1}$$

$Z = 1$ for H-atom

$\therefore E_1$ (Energy of Ist orbit of H-atom)

$$= -2.18 \times 10^{-18} \text{ J atom}^{-1}$$

$$\Delta E = E_4 - E_1$$

$$= \frac{-2.18 \times 10^{-18}}{4^2} - \frac{-2.18 \times 10^{-18}}{1^2}$$

$$= -2.18 \times 10^{-18} \times \left[\frac{1}{4^2} - \frac{1}{1^2}\right]$$

$$\Delta E = -2.18 \times 10^{-18} \times -\frac{15}{16}$$

$$= +2.0437 \times 10^{-18} \text{ J atom}^{-1}$$

$$\therefore \nu = \frac{\Delta E}{h}$$

$$= \frac{2.0437 \times 10^{-18} \text{ J atom}^{-1}}{6.625 \times 10^{-34} \text{ J s}}$$

$$= 3.084 \times 10^{15} \text{ s}^{-1} \text{ atom}^{-1}$$

17. (a) According to de-Broglie's equation,

$$\text{Wavelength } (\lambda) = \frac{h}{mv}$$

where, h = Planck's constant.
Thus, statement (a) is correct.

(b) According to Heisenberg uncertainty principle, the uncertainties of position (Δx) and momentum ($p = m\Delta v$) are related as

$$\Delta x . \Delta p \geq \frac{h}{4\pi} \text{ or, } \Delta x . m\Delta v \geq \frac{h}{4\pi}$$

$$\Delta x . m . \Delta a . \Delta t \geq \frac{h}{4\pi}$$

$$\left[\frac{\Delta v}{\Delta t} = \Delta a,\ a = \text{ acceleration}\right]$$

$$\text{or, } \Delta x \cdot F \cdot \Delta t \geq \frac{h}{4\pi} \qquad [\because F = m \cdot \Delta a]$$

$$\text{or, } \Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

$$[\because \Delta E = F \cdot \Delta x,\ E = \text{ energy}]$$

Thus, statement (b) is correct.

(c) According to Hund's rule the half and fully filled orbitals have greater stability due to greater exchange energy, greater symmetry and more balanced arrangement. Thus, statement (c) is correct.

(d) For a single electronic species like H, energy depends on value of n and does not depend on l. Hence, energy of $2s$-orbital and $2p$-orbital is equal in case of hydrogen like species. Therefore, statement (d) is incorrect.

18. Given, Planck's constant,

$$h = 6.63 \times 10^{-34} \text{ Js}$$

Speed of light, $c = 3 \times 10^{17}$ nm s^{-1}

Frequency of quantum light

$$\nu = 6 \times 10^{15} \text{ s}^{-1}$$

Wavelength, $\lambda = ?$

We know that, $\nu = \dfrac{c}{\lambda}$

or $\lambda = \dfrac{c}{\nu}$

$$= \frac{3 \times 10^{17}}{6 \times 10^{15}}$$

$$= 0.5 \times 10^2 \text{ nm}$$

$$= 50 \text{ nm}$$

19. Given, $\Delta p = 1 \times 10^{-18}$ g cm s^{-1} (uncertainty in momentum)

Mass $= 9 \times 10^{-28}$ g

$$\Delta p = m\Delta v$$

$$1 \times 10^{-18} = 9 \times 10^{-28} \times \Delta v$$

(uncertainty in velocity)

$$\Delta v = 1 \times 10^{9} \text{ cm s}^{-1}$$

20. If $n = 3$,

$l = 0$ to $(3 - 1) = 0, 1, 2$

$m = -l$ to $+l = -2, -1, 0, +1, +2$

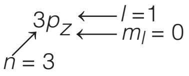
$s = \pm \dfrac{1}{2}$

Therefore, option (c) is not a permissible set of quantum numbers.

21. According to Pauli's exclusion principle, the orbital of the electron having $n = 3, l = 1$ and $m = -1$ is $3p_z$ (as n/m) and an orbital can have a maximum number of two electrons with opposite spins.

$\therefore$ $3p_z$ orbital contains only two electrons or only 2 electrons are associated with $n = 3$, $l = 1$, $m = -1$.

22. The value of $n = 3$ and $l = 1$ suggests that it is a $3p$-orbital while the value of $m_l = 0$ [magnetic quantum number] shows that the given $3p$-orbital is $3p_z$ in nature.



Hence, the maximum number of orbitals identified by the given quantum number is only 1, i.e. $3p_z$.

23. According to Hund's rule of maximum multiplicity, an orbital can accommodate a maximum number of 2 electrons of exactly opposite spin. Hence, option (a) is correct.

Caution Remember, maximum number of electrons in an orbital do not depend upon the quantum numbers as given in the question.

24. According to Aufbau principle, the electrons in an atom are filled in the increasing order of their energies. The order of orbital energies is determined by $(n + l)$ rule. If $(n + l)$ value is same for two orbitals, then the orbital with lower value of n is filled first.

For, $n = 6$

$6s = 6 + 0 = 6$

$6p = 6 + 1 = 7$

$5d = 5 + 2 = 7$

$4f = 4 + 3 = 7$

So, increasing order of energy will be

$$6s \rightarrow 4f \rightarrow 5d \rightarrow 6p.$$

25. Ti ($Z = 22$) electronic configuration

$\Rightarrow$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2 . 3d^2$

According to Aufbau rule

$$3s < 3p < 4s < 3d$$

26. The value of l varies from 0 to $(n - 1)$ and the value of m varies from $-l$ to $+l$ through zero.

The value of 's' $\pm \dfrac{1}{2}$ which signifies the spin of electron. The correct sets of quantum number are following.

n l m s

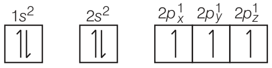
(ii) 2 1 1 $-\dfrac{1}{2}$ (because $l = 2$ is not possible for $n = 2$)

(iv) 1 0 0 $-\dfrac{1}{2}$ (because $m = -1$ is not possible for $l = 0$)

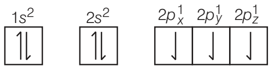
(v) 3 2 2 $+\dfrac{1}{2}$ (because $m = 3$ is not possible for $l = 0$)

27. According to Hund's rule "the pairing of electrons in the orbitals of a particular subshell does not takes place until all the orbitals of a subshell are singly occupied. Moreover, the singly orbitals must have the electrons with parallel spin.

i.e.



or



$\therefore$ Option (a) is the incorrect.

3. *Classification of Elements and Periodicity in Properties*

28. The element with atomic number, $Z = 114$ is flerovium (Fl). It is a super heavy artificial chemical element. In the periodic table of the elements, it is a transactinide element in the p-block. It is a member of the 7th period and is the heaviest known member of the carbon family.

Electronic configuration for $Z = 114$ is

$$[\text{Rn}]\, 5f^{14}, 6d^{10}, 7s^2, 7p^2$$

29. (No option is correct.)

(a) $H^- > H^+ > H$

It is known that radius of a cation is always smaller than that of a neutral atom due to decrease in the number of shells. Whereas, the radius of anion is always greater than a cation due to decrease in effective nuclear charge. Hence, the correct order is

$$H^- > H > H^+$$

(b) $Na^+ > F^- > O^{2-}$

The given species are isoelectronic as they contain same number of electrons. For isoelectronic species,

$$\text{Ionic radii} \propto \frac{1}{\text{atomic number}}$$

Ion: Na^+, F^-, O^{2-}

Atomic number : 11 9 8

Hence, the correct order of ionic radii is $O^{2-} > F^- > Na^+$.

(c) Similarly, the correct option is $O^{2-} > F^- > Na^+$.

(d)

Ions	:	Al^{3+}	Mg^{2+}	N^{3-}
Atomic number	:	13	12	7

Hence, the correct order is,

$N^{3-} > Mg^{2+} > Al^{3+}$

30. A cation has always the lesser ionic size than a metal atom due to loss of electrons and an anion has always the greater size than metal atom due to gain of electrons. The given species are isoelectronic species as they contain same number of electrons.

For isoelectronic species, ionic radii $\propto \frac{1}{\text{atomic number}}$.

Ion	: Ca^{2+}	K^+	Ar	S^{2-}	Cl^-
Atomic no.	20	19	18	16	17

So, the correct order of size is

$Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$

31. Amongst isoelectronic species, ionic radius increases with increase in negative charge or decrease in positive charge.

Atomic radius of the elements decreases across a period from left to right due to increase in effective nuclear charge. On moving down a group, since, number of shells increases, so atomic radius increases.

32. The amount of energy required to remove an electron from unipositive ion is referred as **second ionisation potential**.

In Ti, V, Cr and Mn, generally second ionisation energy increases with increase in atomic number but second ionisation potential of Cr is greater than that of Mn due to the presence of exactly half-filled *d*-subshell in Cr. Thus, the order of second ionisation enthalpy is

Cr > Mn > V > Ti

33. Electron gain enthalpy generally, increases in a period from left to right and decreases in a group on moving downwards. However, members of 3rd period have some what higher electron gain enthalpy as compared to the corresponding members of second period, because of their small size.

O and S belong to VI A (16) group and Cl and F belong to VII A (17) group. Thus, the electron gain enthalpy of Cl and F is higher as compared to O and S.

Cl and F > O and S

Between Cl and F, Cl has higher electron gain enthalpy then the F, since the incoming electron experiences a greater force of repulsion because of small size of F-atom. Similar, it is true in case of O and S, i.e. the electron gain enthalpy of S is higher as compared to O due to its small size. Thus, the correct order of electron gain enthalpy of given elements is O < S < F < Cl.

34. For option (a), first ionisation energy is the energy required to remove an electron from outermost shell.

Hence, correct order is

B < C < O < N.

So, option (a) is incorrect.

For option (b), electron gain enthalpy is the energy required to gain an electron in the outermost shell.

Hence, the correct order is

I < Br < F < Cl.

For option (c), as we move down the group in alkali metal, metallic radius increases Li < Na < K < Rb.

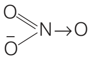
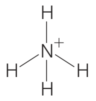
For option (d), in case of isoelectronic species, as positive charge decreases or negative charge increases the ionic size of the species increases and *vice-versa*

$Al^{3+} < Mg^{2+} < Na^+ < F^-$.

35. Generally, acids react with bases and bases (alkalies) react with acids. Sodium hydroxide, NaOH, being a strong alkali never react with a basic oxide (compound). Among the given options, B_2O_3 and BeO are amphoteric oxides, SiO_2 is an acidic oxide and CaO is a basic oxide. Therefore, NaOH does not react with CaO.

4. *Chemical Bonding and Molecular Structure*

36.

Ion	Structure	Hybridisation
NO_2^+	$O{=}\overset{\oplus}{N}{=}O$	*sp*
NO_3^-		sp^2
NH_4^+		sp^3

Thus, option (c) is correct.

37. Molecules having same hybridisation have same number of hybrid orbitals,

$$H = \frac{1}{2}[V + X - C + A]$$

where, V = number of valence electrons of central atom

X = number of monovalent atoms

C = charge on cation

A = charge on anion

$SbCl_5^{2-} = sp^3d^2$, $PCl_5 = sp^3d$

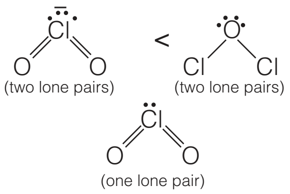
$SF_4 = sp^3d$, $I_3^- = sp^3d$

38. According to VSEPR theory repulsive interaction of electron pairs decreases in the order

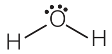
lp – *lp* > *lp* – *bp* > *bp* – *bp*

As the number of lone pairs of electrons increases, bond angle decreases due to repulsion between *lp* – *lp*. Moreover, as the electronegativity of central atom decreases, bond angle decreases.

Hence, the order of bond angle is

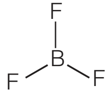


(Cl is less electronegative as compared to O).

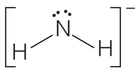
39. (a) $H_2O \Rightarrow$ 

(2 *bp* + 2 *lp*)

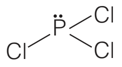
[*bp* = bond pair and *lp* = lone pair]

(b) $BF_3 \Rightarrow$ 

(3 *bp* + 0 *lp*)

(c) $NH_2^- \Rightarrow$ 

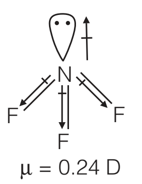
(2*bp* + 2*lp*)

(d) $PCl_3 \Rightarrow$ 

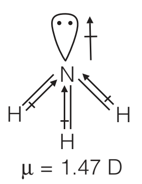
(3 *bp* + 1 *lp*)

Thus, in PCl_3, the central P-atom is surrounded by three bond pairs and one lone pair.

40.



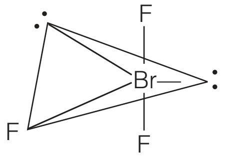
μ = 0.24 D



μ = 1.47 D

F is more electronegative than N, therefore direction of bond is from N to F whereas N is more electronegative than H, the direction of the bond is from H to N. Thus, resultant moment of N—H bonds adds up to the bond moment of lone pair, that of 3N—F bonds partly cancel the resultant moment of lone pair. Hence, the net dipole moment of NF_3 is less than that of NH_3.

41. In BrF_3 molecule, Br is sp^3d hybridised, but its geometry is T-shaped due to distortion of geometry from trigonal bipyramidal to T-shaped by the involvement of lone pair-lone pair repulsion.



42. Paramagnetic species contains unpaired electrons in their molecular orbital electronic configuration.

Molecular orbital configuration of the given species is as :

CO $(6 + 8 = 14) =$

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$$

(All the electrons are paired so, it is diamagnetic).

O_2^- $(8 + 8 + 1 = 17) =$

$$\sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^2 \approx \overset{*}{\pi} 2p_y^1$$

(It contains one unpaired electron so, it is paramagnetic.)

CN^- $(6 + 7 + 1 = 14) =$ same as CO

NO^+ $(7 + 8 - 1 = 14) =$ same as CO

Thus, among the given species only O_2^- is paramagnetic.

43. Molecules with zero bond order, do not exist.

According to molecular orbital theory,

(a) Be_2^+ $(4 + 4 - 1 = 7)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^1$$

$$\text{Bond order (BO)} = \frac{4 - 3}{2} = 0.5$$

(b) Be_2 $(4 + 4 = 8)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2$$

$$\text{BO} = \frac{4 - 4}{2} = 0$$

(c) $B_2 (5 + 5 = 10)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^1 \approx \pi 2p_y^1$$

$$\text{Bond order (BO)} = \frac{6 - 4}{2} = 1$$

(d) Li_2 $(3 + 3 = 6)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2$$

$$\text{BO} = \frac{4 - 2}{2} = 1$$

Thus, Be_2 does not exist under normal conditions.

44. According to the molecular orbital theory (MOT),

$$N_2 (7 + 7 = 14) = \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$$

$$\text{Bond order} = \frac{10 - 4}{2} = 3$$

$N_2^- (7 + 7 + 1 = 15)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1$$

$$\text{BO} = \frac{10 - 5}{2} = 2.5$$

$N_2^{2-} (7 + 7 + 2 = 16)$

$$= \sigma 1s^2, \overset{*}{\sigma} 1s^2, \sigma 2s^2, \overset{*}{\sigma} 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi} 2p_x^1 \approx \overset{*}{\pi} 2p_y^1$$

$$\text{BO} = \frac{10 - 6}{2} = 2$$

Hence, the increasing order of bond order is

$$N_2^{2-} < N_2^- < N_2.$$

45. The molecular orbital configuration of

$$O_2^- (8 + 8 + 1 = 17) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}\ 2p_x^2 \approx \overset{*}{\pi}\ 2p_y^1$$

Bond order (BO)

$$= \frac{N_b - N_a}{2} = \frac{10 - 7}{2} = 1.5$$

$$NO\ (7 + 8 = 15) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2, \sigma 2p_z^2, \pi 2p_x^2 \approx \pi 2p_y^2, \overset{*}{\pi}\ 2p_x^1 \approx \overset{*}{\pi}\ 2p_y^0$$

$$\text{BO} = \frac{10 - 5}{2} = 2.5$$

$C_2^{2-} (6 + 6 + 2 = 14)$

$$= \sigma 1s^2, \overset{*}{\sigma}\ 1s^2, \sigma 2s^2, \overset{*}{\sigma}\ 2s^2, \pi 2p_x^2 \approx \pi 2p_y^2, \sigma 2p_z^2$$

$$\text{BO} = \frac{10 - 4}{2} = 3$$

$$He_2^+ (2 + 2 - 1 = 3) = \sigma 1s^2, \overset{*}{\sigma}\ 1s^1$$

$$\text{BO} = \frac{2 - 1}{2} = \frac{1}{2} = 0.5$$

Hence, order of increasing bond order is

$$He_2^+ < O_2^- < NO < C_2^{2-}$$

5. *States of Matter*

46. For the reaction,

$$SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g),$$

$K_p = 1.6 \text{ atm} = p_{CO_2}$

$= \text{maximum pressure of } CO_2$

Given, $p_1 = 0.4 \text{ atm}, V_1 = 20 \text{L}, T_1 = 400 \text{K}$

$p_2 = 1.6 \text{ atm}, V_2 = ?, T_2 = 400 \text{K}$

At constant temperature, $p_1V_1 = p_2V_2$

$$0.4 \times 20 = 1.6 \times V_2$$

$$V_2 = \frac{0.4 \times 20}{1.6} = 5 \text{ L}$$

47. According to Avogadro's hypothesis, volume of a gas $(V) \propto$ number of moles (n).

Therefore, the ratio of the volumes of gases can be determined in terms of their moles.

$\therefore$ The ratio of volumes of $H_2 : O_2 :$ methane (CH_4) is given by

$$V_{H_2} : V_{O_2} : V_{CH_4} = n_{H_2} : n_{O_2} : n_{CH_4}$$

$$\Rightarrow V_{H_2} : V_{O_2} : V_{CH_4} := \frac{m_{H_2}}{M_{H_2}} : \frac{m_{O_2}}{M_{O_2}} : \frac{m_{CH_4}}{M_{CH_4}}$$

$$\left[\because n = \frac{\text{mass}}{\text{molar mass}}\right]$$

Given, $m_{H_2} = m_{O_2} = m_{CH_4} = m$

$$\text{Thus, } V_{H_2} : V_{O_2} : V_{CH_4} = \frac{m}{2} : \frac{m}{32} : \frac{m}{16} = 16 : 1 : 2$$

48. Equal moles of CO and N_2

$$n_{CO} = n_{N_2}$$

then, according to ideal gas equation, pressure of both gases CO and N_2 becomes equal

$$\therefore \quad p_{CO} = p_{N_2}$$

Given, $p_{CO} + p_{N_2} =$ total pressure of mixture

or $2p_{N_2} = 1 \text{ atm}$ or $p_{N_2} = 0.5 \text{ atm}$

49. Given, number of moles of hydrogen (n_{H_2}) and that of oxygen (n_{O_2}) are equal.

$\therefore$ We have, the relation between ratio of number of moles escaped and ratio of molecular mass.

$$\frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}$$

where, M = molecular mass of the molecule.

$$\Rightarrow \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{2}{32}} \Rightarrow \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{1}{16}}$$

$$\Rightarrow \frac{n_{O_2}}{0.5} = \frac{1}{4} \Rightarrow n_{O_2} = \frac{0.5}{4} = \frac{1}{8}$$

50. Given, $V_A = V_B = 50\,\text{mL}$

$T_A = 150\text{s}, T_B = 200\text{ s}$

$M_B = 36, M_A = ?$

From Graham's law of effusion

$$\frac{r_B}{r_A} = \sqrt{\frac{M_A}{M_B}} = \frac{V_B T_A}{T_B V_A}$$

$$\Rightarrow \quad \sqrt{\frac{M_A}{36}} = \frac{V_A \times 150}{200 \times V_A}$$

or $$\sqrt{\frac{M_A}{36}} = \frac{15}{20} = \frac{3}{4}$$

$$\frac{M_A}{36} = \frac{9}{16}$$

$$M_A = \frac{9 \times 36}{16} = \frac{9 \times 9}{4}$$

$$= \frac{81}{4} = 20.2$$

According to question, no option is correct in this condition,

Note *If* $T_A = 200$ *s and* $T_B = 150$ *s then* $M_A = 64$.

51. Average velocity $= \sqrt{\frac{8RT}{\pi M}}$

$\therefore \quad V_{\text{av}} \propto \sqrt{T}$

or $$\frac{(V_{\text{av}})_2}{(V_{\text{av}})_1} = \sqrt{\frac{2T}{T}} = 1.4$$

52. The extent to which a real gas deviates from ideal behaviour can be understood by a quantity 'Z' called the **compressibility factor**. Easily liquefiable gases like NH_3, SO_2 etc., exhibit maximum deviation from ideal gas as for them $Z <<< 1$.

CH_4 also exhibits deviation but it is less as compared to NH_3.

6. *Thermodynamics*

53. According to first law of thermodynamics,

$$\Delta U = q + W$$

where, ΔU = internal energy

q = heat absorbed or evolved,

W = work done.

Also, work done against constant external pressure (irreversible process).

$$W = -\,p_{\text{ext}}\,\Delta V$$

Work done in irreversible process,

$$W = -\,p_{\text{ext}}\,\Delta V = -\,p_{\text{ext}}\,(V_2 - V_1)$$

$$= -\,2.5\text{ atm }(4.5\text{ L} - 2.5\text{ L})$$

$$= -\,5\text{ L atm} = -\,5 \times 101.3\text{ J}$$

$$= -506.5 \approx -\,505\text{ J}$$

Since, the system is well insulated,

$$q = 0$$

$$\therefore \quad \Delta U = W = -\,505\text{ J}$$

Hence, change in internal energy, ΔU of the gas is – 505 J.

54. Work done $(W) = -\,p_{\text{ext}}\,(V_2 - V_1)$

$= -\,3 \times (6 - 4) = -\,6\text{ L atm}$

$= -\,6 \times 101.32\text{ J}$

$(\because 1\text{ L atm} = 101.32\text{ J})$

$= -\,607.92 \approx -608\text{ J}$

55. Given, $C(s) + O_2(g) \longrightarrow CO_2(g)$;

$\Delta_f H = -\,393.5\text{ kJ mol}^{-1}$

$\because$ Heat released on formation of 44 g or 1 mol

$CO_2 = -395.5\text{kJ mol}$

$\because$ Heat released on formation of 35.2 g of CO_2

$$= \frac{-\,393.5\text{ kJ mol}^{-1}}{44\text{g}} \times 35.2\text{ g}$$

$$= -314.8 \approx -\,315\text{ kJ mol}^{-1}$$

56. $H_2O(l) \xrightarrow{100°\text{ C}} H_2O(g)$

$\Delta_{\text{vap}}H° = \Delta_{\text{vap}}E° + \Delta n_g RT$

$\Delta_{\text{vap}}H°$ = enthalpy of vaporisation

$= 40.66\text{ kJ mol}^{-1}$

For the above reaction,

$$\Delta n_g = n_p - n_r = 1 - 0 = 1$$

$$R = 8.314\text{ JK}^{-1}\text{mol}^{-1}$$

$$T = 100°\text{C}$$

$$= 273 + 100 = 373\text{K}$$

$\therefore$ 40.66 kJ mol^{-1}

$= \Delta_{\text{vap}}E° + 1 \times 8.314 \times 10^{-3} \times 373$

$\Delta_{\text{vap}}E° = 40.66\text{ kJ mol}^{-1} - 3.1\text{kJ mol}^{-1}$

$= +\,37.56\text{ kJ mol}^{-1}$

57. Relation between heat of reaction $(\Delta_r H)$ and bond energies (BE) of reactants and products is given by

$$\Delta_r H = \Sigma\text{BE}_{\text{reactants}} - \Sigma\text{BE}_{\text{products}}$$

The reaction of formation for XY is

$$\frac{1}{2}X_2(g) + \frac{1}{2}Y_2(g) \longrightarrow XY(g);$$

$$\Delta H = -\,200\text{kJ mol}^{-1}$$

Given, the bond dissociation energies of X_2, Y_2 and XY are in the ratio 1 : 0.5 : 1. Let the bond dissociation energies of X_2, Y_2 and XY are 'a' kJ mol^{-1}, $0.5a$ kJ mol^{-1} and 'a' kJ mol^{-1}, respectively.

$\therefore \Delta_r H = \Sigma\text{BE}_{\text{reactants}} - \Delta\,\text{BE}_{\text{products}}$

$$= \left[\frac{1}{2} \times a + \frac{1}{2} \times 0.5a\right] - [1 \times a]$$

$$-200 = \frac{a}{2} + \frac{a}{4} - a$$

$$-200 = \frac{2a + a - 4a}{4} = \frac{-a}{4}$$

$$a = 800\text{ kJ mol}^{-1}$$

$\therefore$ The bond dissociation energy of $X_2 = a\text{ kJ mol}^{-1} = 800\text{ kJ mol}^{-1}$

58. Entropy change is given as,

$$\Delta S = nC_p \ln\frac{T_f}{T_i} + nR\ln\frac{p_i}{p_f} \qquad \ldots\text{(i)}$$

For isothermal process, $T_i = T_f$

$$\therefore \quad nC_p \ln\frac{T_f}{T_i} = nC_p \ln\frac{T_i}{T_i} = 0 \qquad [\ln 1 = 0]$$

From Eq. (i) $\Delta S = nR\ln\frac{p_i}{p_f}$

59. According to Gibbs-Helmholtz equation, Gibbs energy $(\Delta G) = \Delta H - T\Delta S$

where, ΔH = enthalpy change

ΔS = entropy change

T = temperature

For a reaction to be spontaneous

$$\Delta G < 0.$$

$\therefore$ Gibbs -Helmholtz equation becomes,

$$\Delta G = \Delta H - T\Delta S < 0$$

or, $\Delta H < T\Delta S$

or, $$T > \frac{\Delta H}{\Delta S} = \frac{35.5\text{ kJ mol}^{-1}}{83.6\text{ JK}^{-1}\text{mol}^{-1}}$$

$$= \frac{35.5 \times 1000}{83.6} = 425\text{ K}$$

$$T > 425\text{ K}$$

60. We have the Gibbs-Helmholtz reaction for spontaneity as, $\Delta G = \Delta H - T\Delta S$

For reaction to be spontaneous, ΔG must be negative.

For, ΔH should be negative and ΔS should be positive.

$\therefore \quad \Delta H < 0$ and $\Delta S > 0$

And $\Delta S = 0$ shows ΔG a negative quantity.

61. The given phase equilibria is

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

This equilibrium states that, when liquid is heated, it converts into vapour but on cooling, it further converts into liquid, which is derived by Clausius Clapeyron and the relationship is written as,

$$\frac{d\ln p}{dT} = -\frac{\Delta H_v}{RT^2}$$

where, ΔH_v = heat of vaporisation

7. *Equilibrium*

62. For a reaction, $\underset{\text{Reactant}}{A} \rightleftharpoons \underset{\text{Product}}{B}$

$$K = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$$

$$1.6 \times 10^{12} = \frac{[B]_{\text{eq}}}{[A]_{\text{eq}}}$$

$$[B]_{\text{eq}} >> [A]_{\text{eq}} \times 1.6 \times 10^{12}$$

and $[B]_{\text{eq}} > [A]_{\text{eq}}$

So, mostly the product will be present in the equilibrium mixture.

63. Given, $N_2 + 3H_2 \rightleftharpoons 2NH_3, K_1$ ...(i)

$N_2 + O_2 \rightleftharpoons 2NO, K_2$ ...(ii)

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O, \; K_3$ ...(iii)

To calculate,

$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O,$

$K = ?$ ...(iv)

On reversing the equation (i) and multiplying the equation (iii) by 3, we get

$2NH_3 \rightleftharpoons N_2 + 3H_2, \frac{1}{K_1}$ ...(v)

$3H_2 + \frac{3}{2}O_2 \longrightarrow 3H_2O, K_3^3$ ...(vi)

Now, add equation. (ii), (v) and (vi), we get the resultant equation, (iv).

$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$

$\therefore \quad K = \frac{K_2 K_3^3}{K_1}$

64. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$

$K = \frac{[Fe^{3+}][OH^-]^3}{[Fe(OH)_3]}$ ...(i)

Let the concentration of Fe^{3+} is increased by x times and the concentration of OH^- decreases by $\frac{1}{4}$ times.

$K = \frac{[xFe^{3+}][\frac{1}{4} \times OH^-]^3}{[Fe(OH)_3]}$ ...(ii)

On dividing Eq. (ii) by (i) we get

$\frac{1}{64} \times x = 1 \Rightarrow x = 64$ times

65. $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

	$2AB_2(g)$	$2AB(g)$	$B_2(g)$
Initial moles	1	0	0
At equil.	$2(1-x)$	$2x$	x

where, x = degree of dissociation.

Total moles at equilibrium

$= 2 - 2x + 2x + x = (2 + x)$

So, $p_{AB_2} = \frac{2(1-x)p}{(2+x)},$

$p_{AB} = \frac{2xp}{(2+x)}$

$p_{B_2} = \frac{xp}{(2+x)}$

$$K_p = \frac{(p_{AB})^2(p_{B_2})}{(p_{AB_2})^2}$$

$$= \frac{\left(\frac{2xp}{2+x}\right)^2\left[\left(\frac{x}{2+x}\right)p\right]}{\left[\left(\frac{2(1-x)}{(2+x)}\right)p\right]^2}$$

$$= \frac{4x^3p^3}{(2+x)^3} \times \frac{(2+x)^2}{p^2 4(1-x)^2}$$

$$= \frac{x^3p}{(2+x)(1-x)^2}$$

$$= \frac{x^3p}{2} \quad [\because x <<< 1 \text{ and } 2]$$

$$x = \left(\frac{2K_p}{p}\right)^{1/3} \quad \text{so, } \begin{matrix}(1-x) \approx 1 \\ (2+x) \approx 2\end{matrix}$$

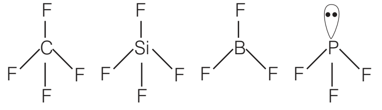
66. $X_2(g) + 4Y_2 \rightleftharpoons 2XY_4(g)$

where, $\Delta H < 0$ and $\Delta n < 0$

$[\Delta n = n_P - n_R]$

$\therefore$ The forward reaction is favoured at high pressure and low temperature. (According to Le-Chatelier's principle)

67. The molecule with lone pair at centre atom, will behave as Lewis base. In the given molecules, only PF_3 has lone pair at P as shown below:



Thus, PF_3 acts as a Lewis base (electron-pair donor due to presence of lone pair on P-atom).

68. Given, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+,$

$K_a = 1.5 \times 10^{-5}$ ...(i)

$HCN \rightleftharpoons H^+ + CN^-,$

$K_{a_1} = 4.5 \times 10^{-10}$ ...(ii)

For $CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$

$K = ?$

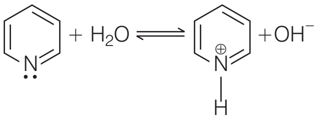
On subtracting Eq. (ii) from Eq. (i), we get

$CH_3COOH + CN^- \rightleftharpoons HCN + CH_3COO^-$

$$K = \frac{K_a}{K_{a_1}} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}}$$

$$= \frac{10^5}{3} = 3.33 \times 10^4 \approx 3 \times 10^4$$

69. The percentage of pyridine can be equal to the percentage of dissociation of pyridinium ion and pyridine solution as shown below:



As pyridinium is a weak base, so degree of dissociation is given as

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7 \times 10^{-9}}{0.10}}$$

$$= \sqrt{1.7 \times 10^{-8}} = 1.3 \times 10^{-4}$$

or, percentage of dissociation

$= (\alpha \times 100)\%$

$= (1.3 \times 10^{-4}) \times 100$

$= 0.013\%$

70. The highest pH refers to the basic solution containing OH^- ions. Therefore, the basic salt releasing more OH^- ions on hydrolysis will give highest pH in water.

Only the salt of strong base and weak acid would release more OH^- ion on hydrolysis. Among the given salts, Na_2CO_3 corresponds to the basic salt as it is formed by the neutralisation of NaOH [strong base] and H_2CO_3 [weak acid].

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

71. 75 mL $\frac{M}{5}$ HCl + 25 mL $\frac{M}{5}$ NaOH

Milliequivalent of HCl

$= 75 \text{ mL of } \frac{M}{5} \text{ HCl} = \frac{1}{5} \times 75 = 15$

Milliequivalent of NaOH

$= 25 \text{ mL of } \frac{M}{5} \text{ NaOH}$

$= \frac{1}{5} \times 25 = 5$

$\therefore$ Milliequivalent of HCl left unused

$= 15 - 5 = 10$

Volume of solution = 100 mL

$\therefore$ Molarity of $[H^+]$ in the resulting mixture

$= \frac{10}{100} = \frac{1}{10}$

$\therefore \quad pH = \log\frac{1}{[H^+]} = \log(10) = 1$

72. Given, K_a $(NH_4OH) = 1.77 \times 10^{-5}$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$K_a = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.77 \times 10^{-5}$ ...(i)

Hydrolysis of NH_4Cl takes place as,

$NH_4Cl + H_2O \longrightarrow NH_4OH + HCl$

or $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

Hydrolysis constant,

$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]}$ ...(ii)

or $\quad K_h = \frac{[NH_4OH][H^+][OH^-]}{[NH_4^+][OH^-]}$ ...(iii)

From Eqs. (i), (ii) and (iii)

$K_h = \frac{K_w}{K_a} \quad [\because [H^+][OH^-] = K_w]$

$= \frac{10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}$

73. For a general reaction,

$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

Solubility product

$(K_{sp}) = [A^{y+}]^x \, [B^{x-}]^y$

For $BaSO_4$ (binary solute giving two ions)

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$\therefore K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$

$= (S)\,(S) = S^2$ ...(i)

[where, S = solubility]

Given, $S = 2.42 \times 10^{-3}\ gL^{-1}$

Molar mass of $BaSO_4$ = 233 g mol^{-1}

∴ Solubility of $BaSO_4$

$$(S) = \frac{2.42 \times 10^{-3}}{233}\ mol\ L^{-1}$$

$= 1.04 \times 10^{-5}\ mol\ L^{-1}$

On substituting the value of S in Eq. (i), we get

$K_{sp} = (1.04 \times 10^{-5}\ mol\ L^{-1})^2$

$= 1.08 \times 10^{-10}\ mol^2\ L^{-2}$

74. $\Delta G°$ is related to K_{sp} by the equation,

$\Delta G° = -\,2.303RT \log K_{sp}$

Given, $\Delta G° = +\,63.3$ kJ

$= 63.3 \times 10^3$ J

Thus, substitute $\Delta G° = 63.3 \times 10^3$ J, $R = 8.314\ JK^{-1}\ mol^{-1}$ and $T = 298$ K [25 + 273 K] from the above equation we get,

$63.3 \times 10^3 = -2.303 \times 8.314 \times 298 \log K_{sp}$

$\therefore \log K_{sp} = -11.09$

$\Rightarrow K_{sp} = \text{antilog}\,(-\,11.09)$

$K_{sp} = 8.0 \times 10^{-12}$

8. *Redox Reactions*

75. The given redox reaction is

$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$

The reaction can be balanced by considering the following steps:

***Step* I** Balance the atoms except H and O.

$MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + 2CO_2 + H_2O$

***Step* II** Write the oxidation number of each atom.

Oxidation $(-2e^-)$

$\overset{+7}{Mn}O_4^- + \overset{+6}{C_2}O_4^{2-} + H^+ \rightarrow Mn^{2+} + 2\overset{+8}{C}O_2 + H_2O$

Reduction $(+5e^-)$

***Step* III** Cross multiply by change in oxidation number

$\overset{+7}{Mn}O_4^- \longrightarrow Mn^{2+};\ 5e^-$ gain

$\overset{+6}{C_2}O_4^{2-} \longrightarrow \overset{+8}{2CO_2};\ 2e^-$ loss

$2MnO_4^- + 5C_2O_4^- + H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + H_2O$

***Step* IV** Balance oxygen by adding H_2O on deficient site.

$2MnO_4^- + 5C_2O_4^{2-} + H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

***Step* V** Balance hydrogen

$2MnO_4^{2-} + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

∴ The coefficients of the reactants, MnO_4^-, $C_2O_4^{2-}$ and H^+ are 2, 5 and 16, respectively.

76. (i) $Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2 + O_2$

(ii) $2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2Cr_2O_4 + Cr_2O_3 + \frac{3}{2}O_3$

(iii) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

(iv) $KClO_3 \xrightarrow{\Delta} KCl + \frac{3}{2}O_2$

77. In peroxides, the oxidation state of O is –1 and gives H_2O_2 with dilute acids and have peroxide linkage. In KO_2,

$+\,1 + (x \times 2) = 0$

$x = \frac{-1}{2}$

(thus, it is a superoxide, not a peroxide) In BaO_2, $+\,2 + (x \times 2) = 0$

$x = -\,1$

Thus, it is a peroxide and gives H_2O_2 when reacts with dilute acids and has peroxide linkage as

$Ba^{2+}\ [O - O]^{2-}$
$\uparrow$
Peroxide linkage

In MnO_2 and NO_2, Mn and N exhibit variable oxidation states, thus, the oxidation state of O in these is – 2. Hence, these are not peroxides. Thus, it is clear that among the given molecules only BaO_2 is a peroxide.

78. When chlorine gas reacts with hot and conc. NaOH solution, it disproportionates into (Cl^-) chloride and (ClO_3^-) chlorate ions.

Oxidation

$3\overset{0}{Cl_2} + 6NaOH \longrightarrow 5\,NaCl^{-1} + Na\overset{+5}{Cl}O_3 + 3H_2O$

Reduction

In this process, oxidation number of chlorine changes from 0 to –1 and 0 to +5.

79. HCl and SO_2 are reducing agents which can reduce MnO_4^{2-}, CO_2 which is neither oxidising nor reducing will provide only acidic medium. It can shift reaction in forward direction and reaction can go to completion.

9. *Hydrogen*

80.
- For ionic salts, hydrogen never behaves as cation, but behaves as anion (H^-).
- H_3O^+ exists freely in solution.
- Dihydrogen acts as a reducing agent.
- Hydrogen has three isotopes.
  (i) Protium $({}_1^1H)$ (ii) Deuterium $({}_1^2H)$
  (iii) Tritium $({}_1^3H)$
  Protium is the most common isotopes of hydrogen with an abundance of 99.98%.

81. In the reaction,

Oxidation

$\overset{+1\ -1}{H_2O_2} + \overset{0,-2}{O_3} \longrightarrow \overset{+1,\ -2}{H_2O} + 2\overset{0}{O_2}$

Reduction

Since, H_2O_2 oxidises O_3 to O_2 and behaves as an oxidising agent.

Further, in the reaction,

$\overset{+1\ -1}{H_2O_2} + \overset{+1\ -2}{Ag_2O} \longrightarrow 2\overset{0}{Ag} + \overset{+1\ -2}{H_2O} + \overset{0}{O_2}$

Reduction

Oxidation

Here, H_2O_2 reduces Ag_2O into metallic silver (Ag) (as oxidation number is reducing from +1 to 0).

10. *s-block Elements*

82. The smaller the size of the ion, the greater is the degree of hydration, thus degree of hydration is highest for Li^+ and lowest for Cs^+. Thus, Li^+ holds more water molecules in its hydration sphere and becomes largest in size among alkali metals and Cs^+ ion hold least number of water molecules. Hence, ionic mobility is highest for Cs^+ (due to its smallest size in aqueous solution) and lowest for Na^+. Thus, the order of ionic mobility in aqueous solution is

$Cs^+ > Rb^+ > K^+ > Na^+$

83. As the size of the alkali metal cation increases, thermal stability of their hydrides decreases.

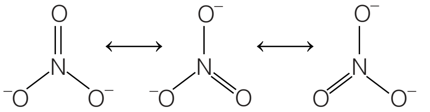
Hence, the correct order of thermal stability of alkali metal hydrides is

LiH > NaH > KH > RbH > CsH

84. Metals are usually not found as nitrates in their ores, because metal nitrates are highly soluble in water. For example, KNO_3 (salt peter) would be classified as completely soluble. Thus, KNO_3 could be expected to dissociate completely in aqueous solution to give K^+ and NO_3^- ions.

$$KNO_3 \rightleftharpoons K^+(aq) + NO_3^-(aq)$$

The nitrate anion has three equivalent oxygen surrounding a central nitrogen atom. This tends to spread the single negative charge and make it easier for water (using hydrogen bonds) to separate the ions in solution.



85. The covalent character in an ionic bond can be decided by Fajan's rule.

According to this rule, compounds with small cation, large anion, more charge on cation or anion shows more covalent character. As the above conditions opposes, it shows ionic character.

Since, the size of cation decreases in the order $Ba^{2+} > Ca^{2+} > Be^{2+}$.

Therefore, the correct order of ionic character will be

$$BeH_2 < CaH_2 < BaH_2.$$

BeH_2 has some covalent character. It is because of the effect of polarisation. According to Fajan's rule, smaller the size of cation and more the charge on the cation, greater is its polarising power. Thus, BeH_2 has some covalent character also.

86. All salts are soluble in water and give strong acid and weak base.

$$SrCl_2 + 2H_2O \longrightarrow Sr(OH)_2 + 2HCl$$
$$BaCl_2 + 2H_2O \longrightarrow Ba(OH)_2 + 2HCl$$
$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
$$CaCl_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2HCl$$

The basic nature of alkaline earth metals generally increases from Be to Ra. Thus, the order of basic nature of these hydroxides is

$$Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$

Hence, pH is highest for $BaCl_2$. (As pH increases with basic nature)

87. **Solubility of the sulphates**. The sulphates become less soluble as you go down the group. i.e.

$$Mg > Ca > Sr > Ba$$

The magnitude of the lattice energy remains almost constant as the size of the sulphate ion is so big that small increase in the size of the cation from Be to Ba does not make any difference. However, the hydration energy decreases from Be^{2+} to Ba^{2+} appreciably as the size of the cation increases down the group. The significantly high solubility of $MgSO_4$ is due to high enthalpy of solvation of the smaller Mg^{2+} ions.

88. Hydration energy of sulphate decreases from top to bottom in II group. Mg^{2+} is smaller than other given ions of II group, so Mg^{2+} is readily hydrated. $MgSO_4$ has higher hydration energy than lattice energy.

89. When calcium carbide (CaC_2) reacts with nitrogen (N_2) under high temperature, it forms calcium cyanamide which is also called **nitrolim**.

$$CaC_2(s) + N_2(g) \xrightarrow[\text{temperature}]{\text{High}} \underset{\text{Calcium cyanamide}}{Ca(CN)_2(s)} + C(s)$$

90. Compound X is $CaCO_3$.

$$\underset{X}{CaCO_3} \xrightarrow{\Delta} \underset{\text{Residue}}{CaO} + CO_2\uparrow$$
$$\underset{\text{Residue}}{CaO} + H_2O \longrightarrow \underset{Y}{Ca(OH)_2}$$
$$\underset{Y}{Ca(OH)_2} + \underset{\text{Excess}}{CO_2} + H_2O \longrightarrow \underset{Z}{Ca(HCO_3)_2}$$
$$\underset{Z}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{X}{CaCO_3} + H_2O + CO_2\uparrow$$

11. *Some p-block Elements*

91. The atomic radii as well as ionic radii increases on moving down the group 13 elements because of the successive addition of one extra shell of electrons.
However, there is an anomaly at gallium in case of atomic radii. Atomic radii of Ga is lesser as compared to Al. Gallium (Ga) with electronic configuration, $[Ar]_{18}3d^{10}4s^2 4p^1$ has an extra d-electrons which do not screen the nucleus effectively. Consequently, electrons of Ga are more attracted by nucleus.
Thus, the increasing order of atomic radii of the group 13 elements is B (85 pm) < Ga (135 pm) < Al (143 pm) < In (167 pm) < Tl (170 pm).

92. As the size of halogen atom increases, the acidic strength of boron halides increases.

Thus, BF_3 is the weakest Lewis acid. This is because of the $p\pi$-$p\pi$ back bonding between the fully filled unutilised $2p$-orbitals of F and vacant $2p$-orbitals of boron which makes BF_3 less electron deficient. Such back donation is not possible in case of BCl_3 or BBr_3 due to larger energy difference between their orbitals. Thus, these are more electron deficient. Since, on moving down the group the energy difference increases, the Lewis acid character also increases. Thus, the tendency to behave as Lewis acid follows the order

$$BBr_3 > BCl_3 > BF_3.$$

93. Al_2O_3 may be converted into anhyd. $AlCl_3$ by heating a mixture of Al_2O_3 and carbon in dry chlorine.

$$Al_2O_3 + 3C + \underset{\text{Hot and dry}}{3Cl_2} \longrightarrow \underset{\text{Anhy. }AlCl_3}{Al_2Cl_6}$$

Anhy. $AlCl_3$ exists in the form of dimer as Al_2Cl_6.

94. Al^{3+} shows maximum coordination number 6, thus it will form AlF_6^{3-}.

AlF_3 forms $K_3[AlF_6]$ when dissolved in HF in the presence of KF as shown below.

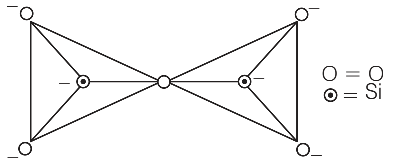
$$AlF_3 + 3KF \xrightarrow{HF} K_3[AlF_6]$$

95. Boric acid can be considered as an acid because its molecule accepts OH^- from water, releasing proton.

$$\underset{\text{Acid}}{H_3BO_3} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{base}}}{B(OH)_4^-} + \underset{\substack{\text{Conjugate}\\\text{acid}}}{H^+}$$

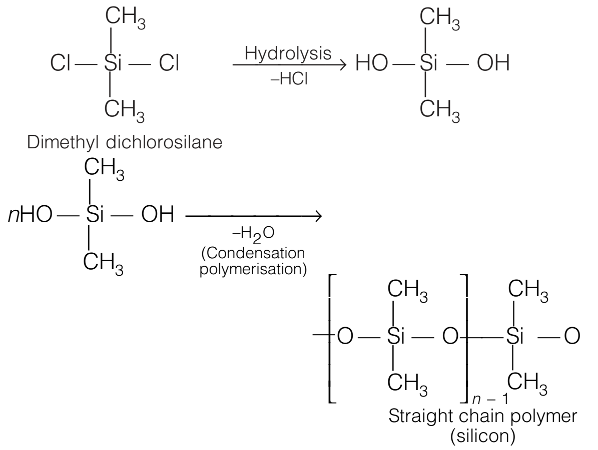
96. The inability of ns^2 electrons of the valence shell to participate in bonding is called as inert pair effect. Due to this effect, the lower oxidation state becomes more stable on descending the group. Thus, Sn^{2+} is a reducing agent while Pb^{4+} act as an oxidising agent.

97. In pyrosilicate, only one oxygen atom is shared.



Pyrosilicate

98.



$$Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow[-HCl]{\text{Hydrolysis}} HO-\overset{CH_3}{\underset{CH_3}{Si}}-OH$$

Dimethyl dichlorosilane

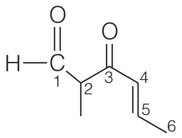
$$nHO-\overset{CH_3}{\underset{CH_3}{Si}}-OH \xrightarrow[\text{(Condensation polymerisation)}]{-H_2O} -\!\!\left[O-\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_{n-1}\!\!-\overset{CH_3}{\underset{CH_3}{Si}}-O$$

Straight chain polymer (silicon)

Straight chain silanes are silicon oils. These are more stable at high temperature than mineral oils and have less tendency to thicken at low temperature.

12. *Organic Chemistry : Some Basic Principles and Techniques*

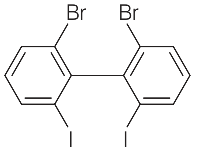
99.



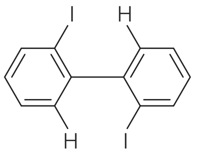
—CHO group gets higher priority over $>C=O$ and $>C=C<$ group in numbering of principal carbon chain.

IUPAC name = 3-keto-2-methylhex-4-enal.

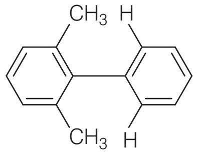
100. The biphenyl compounds having proper substitution at *ortho*-position of benzene rings resulting steric hindrance. This steric hindrance makes the biphenyl system non-planar and hence optically active compounds.



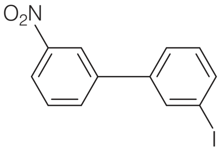
- Proper substitution
- Restricted rotation about single bond



- Improper substitution

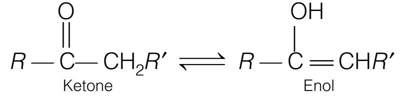


- Improper substitution



- No bulkier group present at *ortho* position arising improper substitution

101. In keto-enol tautomerism, a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol.

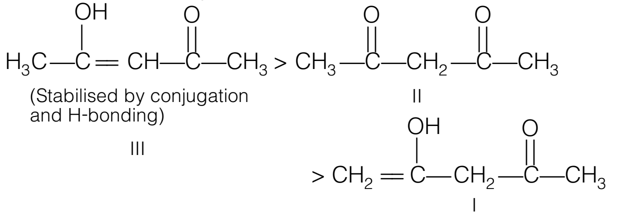


$$R-\overset{O}{\overset{\|}{C}}-CH_2R' \rightleftharpoons R-\overset{OH}{\overset{|}{C}}=CHR'$$

Ketone Enol

(containing α-hydrogen)

102. The enols of β-dicarbonyl compounds are more stable because of conjugation and intramolecular H-bonding. Thus, the order of stability is



$$H_3C-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-CH_3 > CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 > CH_2=\overset{OH}{\overset{|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

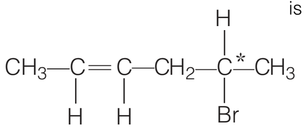
(Stabilised by conjugation and H-bonding)
III

II

I

Less stable as (=) bond is not in conjugation with carbonyl group

103.



$$CH_3-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-CH_2-\overset{H}{\underset{Br}{\overset{|}{\underset{|}{C^*}}}}-CH_3$$

C* = asymmetric carbon

Number of optical isomers = 2^n

where, n = number of asymmetric carbon atoms = $2^1 = 2$

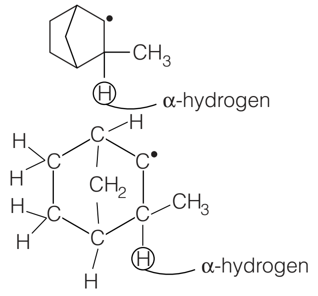
Number of geometrical isomers = 2^n

where, n = number of double bonds = $2^1 = 2$

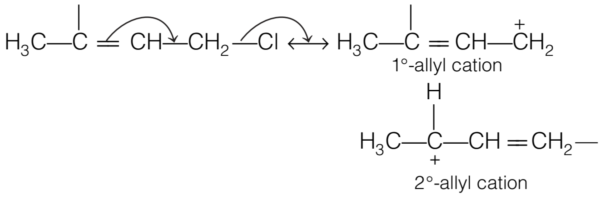
Hence, total number of stereoisomers = Total optical isomers + Total geometrical isomers = 2+ 2 = 4

104. Hyperconjugation occurs through the H-atoms present on the carbon atom next to the double bond, i.e. α-hydrogen atoms. There is no α-H in the structures I and II.

So, hyperconjugation occurs in structure III only. i.e.



105. Allylic and benzylic halides show high reactivity towards S_N1 reaction. Further, due to greater stabilisation of allyl and benzyl carbocations intermediates by resonance, primary allylic and primary benzylic halides show higher reactivity in S_N1 reactions than other simple primary halides.



$$H_3C-\overset{H}{\overset{|}{C}}=CH-CH_2-Cl \longleftrightarrow H_3C-\overset{H}{\overset{|}{C}}=CH-\overset{+}{C}H_2$$

1°-allyl cation

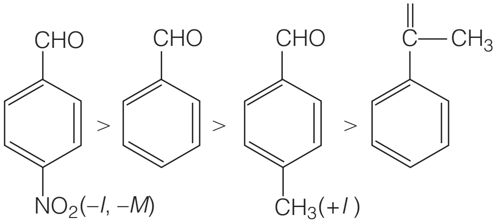
$$H_3C-\overset{H}{\overset{|}{\underset{+}{C}}}-CH=CH_2-$$

2°-allyl cation

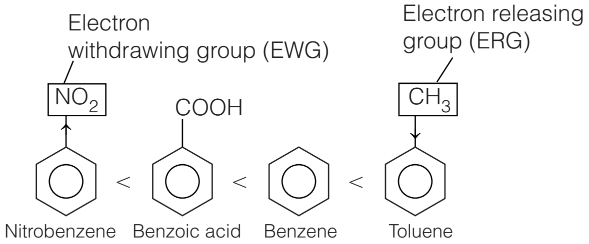
Hence, it undergoes nucleophilic reaction readily.

106. Reactivity of carbonyl compounds toward nucleophilic addition reactions depends on the presence of substituted group.

Electron withdrawing (–*I*, – *M*) groups increase reactivity towards nucleophilic addition reactions. Thus, correct order is



107. Presence of electron releasing groups like —*R*, —OH etc., increases the electron density at *o*/*p*-position and thus, makes the benzene ring more reactive (at *o*/*p*-positions) towards an electrophile. On the other hand, electron withdrawing groups like —COOH, —NO_2 etc., if present, reduces electron density and thus, reduces the activity of benzene nucleus towards an electrophile. Thus, the order of the given compounds toward electrophilic nitration is

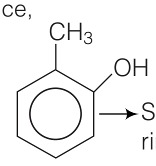


Thus, toluene is most reactive towards electrophilic nitration.

108. Electron withdrawing substituent deactivates the benzene nucleus towards electrophilic substitution while electron releasing substituent activates the ring towards electrophilic substitution.

Among the given, —OH has the higher electron donating tendency and thus, activates the ring more towards electrophilic substitution.

Hence,

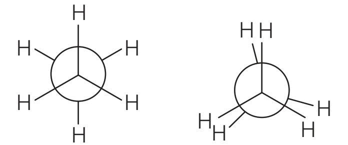


Show + *M*-effect, due to this benzene ring becomes activate.

It is more reactive towards electrophilic reagent.

13. *Hydrocarbons*

109. Due to the absence of torsional strain staggered conformation of ethane is more stable than eclipsed conformation of it.



Staggered conformation Eclipsed conformation

110. The given reaction takes place as follows :

$$\underset{(A)}{CH_4} \xrightarrow[\text{Step I}]{Br_2\ /h\nu} CH_3Br \xrightarrow[\substack{\text{Wurtz reaction}\\ \text{(Step II)}}]{\text{Na/dry ether}} \underset{(A)}{CH_3—CH_3}$$

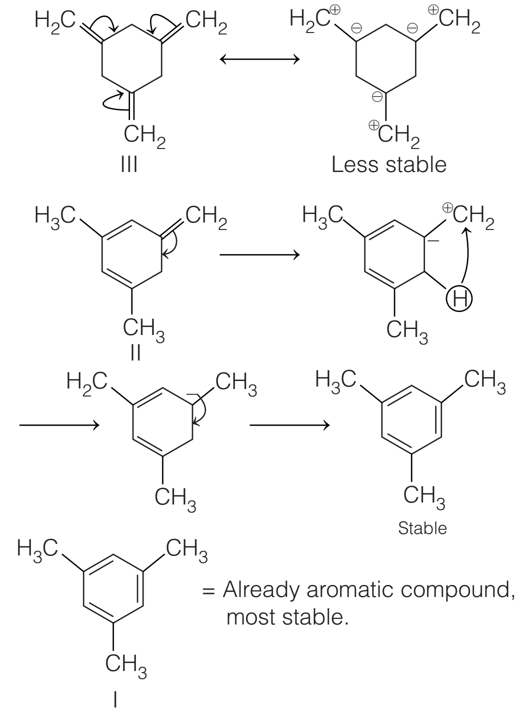
***Step* I** Alkyl halide is formed by free radical halogenation of alkane in the presence of UV-light.

***Step* II** The formed alkyl halide reacts with sodium in presence of dry ether to form alkane containing double number of carbon atoms present in alkyl halide.

This reaction is known as Wurtz reaction.

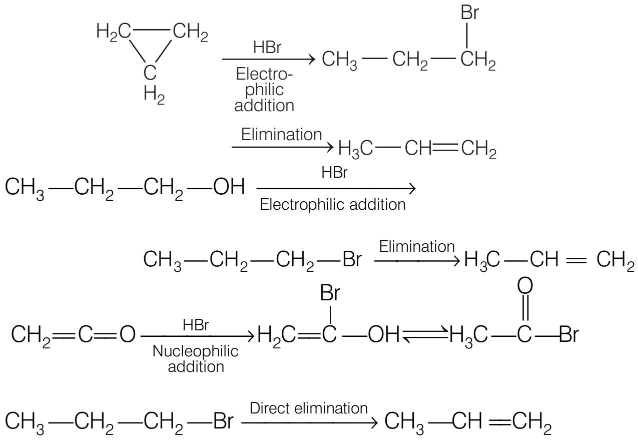
From the above mechanism, it is concluded that option (*d*) is correct as in all other cases the hydrocarbon formed in step 2 will contain more than four carbon atoms.

111. The enthalpy of hydrogenation of given compounds is inversely proportional to stability of alkene.



Hence, correct order is I>II>III.

112. The said reactions can be visualised as :



$$CH_3—CH_2—CH_2—Br \xrightarrow{\text{Elimination}} H_3C—CH=CH_2$$

$$CH_2=C=O \xrightarrow[\text{addition}]{\substack{HBr\\ \text{Nucleophilic}}} H_2C=\overset{\overset{\displaystyle Br}{|}}{C}—OH \rightleftharpoons H_3C—\overset{\overset{\displaystyle O}{\|}}{C}—Br$$

$$CH_3—CH_2—CH_2—Br \xrightarrow{\text{Direct elimination}} CH_3—CH=CH_2$$

Thus, option (c) is correct.

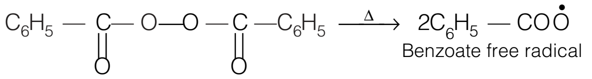
113. Reaction of HBr with propene in the presence of peroxide gives *n*-propyl bromide. This addition reaction is an example of anti-Markownikoff's addition reaction.

(i.e. it is completed in form of free radical addition)

$$CH_3-CH=CH_2+HBr\xrightarrow{\text{Peroxide}}\underset{n\text{-propyl bromide}}{CH_3-CH_2-CH_2Br}$$

Mechanism of this reaction is represented as follows :

***Step* I** Formation of free radical of peroxide by means of decomposition.



$$C_6H_5-\overset{\displaystyle O}{\underset{}{C}}-O-O-C(=O)-C_6H_5\xrightarrow{\Delta}2C_6H_5-CO\dot{O}$$

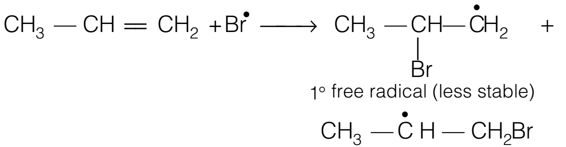
Benzoyl peroxide

Benzoate free radical

***Step* II** Benzoate free radical forms bromine free radical with HBr.

$$C_6H_5CO\dot{O}+H-Br\longrightarrow C_6H_5COOH+\dot{Br}$$

***Step* III** Bromine free radical attacks on C═C of propene to form intermediate free radical.



$$CH_3-CH=CH_2+\dot{Br}\longrightarrow \underset{1^\circ\text{ free radical (less stable)}}{CH_3-\underset{\displaystyle Br}{CH}-\dot{C}H_2}+\underset{2^\circ\text{ free radical (more stable)}}{CH_3-\dot{C}H-CH_2Br}$$

1° free radical (less stable)

2° free radical (more stable)

Hence, $CH_3-\dot{C}H-CH_2Br$ is the major product of this step.

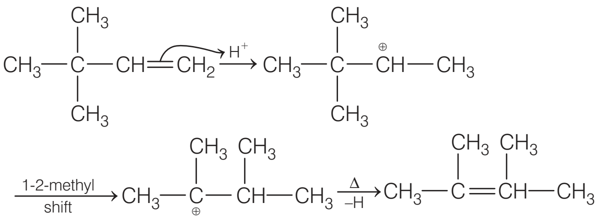
***Step* IV** More stable free radical accept hydrogen free radical from benzoic acid and give final product of reaction. i.e. *n*-propyl bromide.

$$CH_3-\dot{C}H-CH_2Br+C_6H_5COOH\longrightarrow \underset{n\text{-propyl bromide}}{CH_3-CH_2-CH_2Br}+C_6H_5CO\dot{O}$$

***Step* V** Benzoate free radicals are changed into benzoyl peroxide for the termination of free radical chain.

$$C_6H_5CO\dot{O}+C_6H_5CO\dot{O}\longrightarrow(C_6H_5COO)_2$$

114.



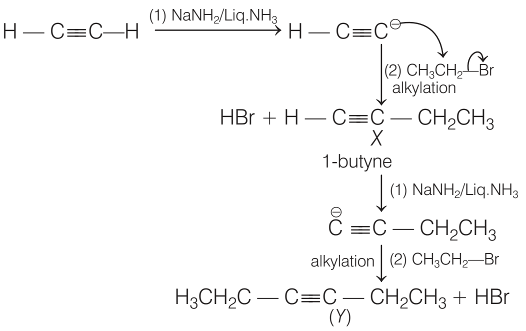
$$CH_3-C(CH_3)_2-CH=CH_2\xrightarrow{H^+}CH_3-C(CH_3)_2-\overset{\oplus}{C}H-CH_3\xrightarrow[\text{shift}]{\text{1-2-methyl}}CH_3-\overset{\oplus}{C}(CH_3)-CH(CH_3)-CH_3\xrightarrow[-H]{\Delta}CH_3-C(CH_3)=C(CH_3)H-CH_3$$

115. Greater the *s*-character of C-atom in hydrocarbons, greater the electronegativity of that carbon and thus greater the acidic nature of the H attached to electronegative carbon.

	$CH\equiv CH$	$CH_2=CH_2$	CH_3-CH_3
Hybridisation :	*sp*	sp^2	sp^3
s-character :	50%	33%	25%
Electronegativity :	← Max.		
Acidic character of terminal H	← Max.		

Thus, $CH\equiv CH>CH_3C\equiv CH>CH_2=CH_2>CH_3-CH_3$

116. Since, $NaNH_2$/liq.NH_3 behaves as a base, so it abstracts proton from acetylene to form acetylide anion followed by alkylation to give compound (*X*), i.e. 1-butyne. (*X*) further reacts with $NaNH_2$/liq.NH_3 followed by alkylation with ethyl bromide yields 3-hexyne (*Y*).



$$H-C\equiv C-H\xrightarrow{(1)\ NaNH_2/Liq.NH_3}H-C\equiv C^{\ominus}\xrightarrow[\text{alkylation}]{(2)\ CH_3CH_2-Br}HBr+H-C\equiv C-CH_2CH_3\ (X)$$

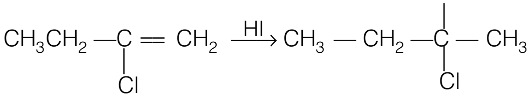
1-butyne

$$\xrightarrow{(1)\ NaNH_2/Liq.NH_3}\overset{\ominus}{C}\equiv C-CH_2CH_3\xrightarrow[\text{alkylation}]{(2)\ CH_3CH_2-Br}H_3CH_2C-C\equiv C-CH_2CH_3+HBr\ (Y)$$

3-hexyne

117. Followed by Markownikoff's rule.

$$CH_3-CH_2-C\equiv CH+HCl\longrightarrow$$

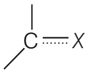


$$CH_3CH_2-\underset{\displaystyle Cl}{C}=CH_2\xrightarrow{HI}CH_3-CH_2-\overset{\displaystyle I}{\underset{\displaystyle Cl}{C}}-CH_3$$

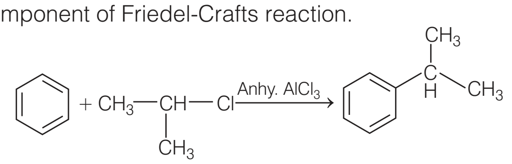
2-chloro-2-iodobutane

118. In chlorobenzene, bromobenzene and chloroethene, lone pair of halogen is delocalised with π-bonds so it attains double bond character. Thus, these are not suitable as a halide component for Friedel-Crafts reaction.

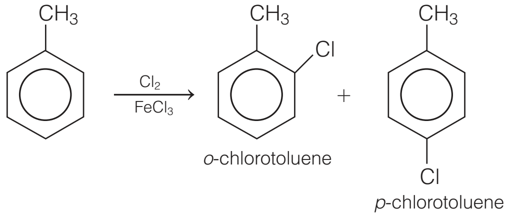
Halides, i.e. chloro and bromobenzene along with chloroethene have carbon halogen bond as :



But this is not a case with isopropyl chloride and used as component of Friedel-Crafts reaction.



119. In the presence of halogen carrier, electrophilic substitution occurs while in the presence of sunlight, substitution, occurs at the side chain.



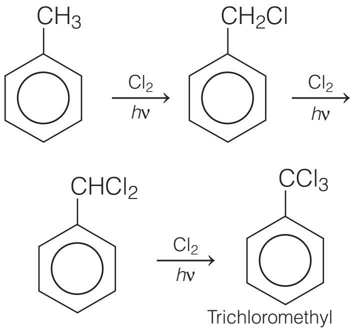
o-chlorotoluene

p-chlorotoluene (*X*)

$$FeCl_3+Cl_2\longrightarrow FeCl_4^-+\underset{\text{Electrophile attacking species}}{Cl^+}$$

(∵—CH_3 is an *o*/*p*-directing group.)

In presence of $h\nu$, reaction is free radical substitution reaction.



Trichloromethyl benzene
(*Y*)

14. *Environmental Chemistry*

120. Microorganisms present in the soil act as biggest source and sink. A sink is a natural or artificial reservoir that accumulates and stores some chemical compound for an indefinite period. Thus, (b) is correct option.

121. Among the given chlorofluorocarbons are the compounds that are responsible for the ozone depletion which degrade ozone into moleculer oxygen. It is not a component of photochemical smog while other are component of smog.

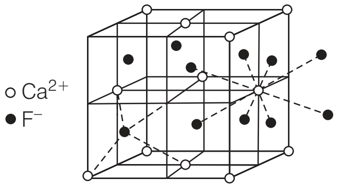
122. The fish growth is inhibited, if the dissolved concentration of oxygen in water is below 6 ppm.

123. N_2O (nitrous oxide) occurs naturally in the environment.

In an automobile engine, when fuel is burnt dinitrogen and dioxygen combine to yield NO and NO_2.

15. *Solid State*

124. In CaF_2 (fluorite structure), Ca^{2+} ions are arranged in ccp arrangement (Ca^{2+} ions are present at all corners and at the centre of each face of the cube) while F^- ions occupy all the tetrahedral sites.



From the above figure, you can clearly see that coordination number of F^- is 4 while that of Ca^{2+} is 8.

125. Volume of atoms in a unit cell

$$(V) = \frac{4}{3}\pi r^3$$

For primitive cell, $r = \frac{a}{2}$

$$V = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}$$

Volume of the unit cell $(V) = a^3$

Thus, total volume occupied by the atoms

$$= \frac{\text{Volume of the atoms in unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{\pi a^3}{6} \times \frac{1}{a^3} = \frac{\pi}{6} = 0.52$$

126. In bcc unit cell, the number of atoms = 2

Thus, volume of atoms in unit cell

$$(V) = 2 \times \frac{4}{3}\pi r^3$$

For bcc structure $(r) = \frac{\sqrt{3}}{4}a$

$$(V) = 2 \times \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3 = \frac{\sqrt{3}}{8}\pi a^3$$

Volume of unit cell $(V) = a^3$

Percentage of volume occupied by unit cell

$$= \frac{\text{Volume of the atoms in unit cell}}{\text{Volume of unit cell}}$$

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

Hence, the free space in bcc unit cell = 100 − 68 = 32%

127. If a = edge length of cubic systems

For simple cubic structure,

radius $= \frac{a}{2}$

For body centred cubic structure,

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

For face centred cubic structure,

radius $= \frac{a}{2\sqrt{2}}$

Hence, the ratio of radii

$$= \frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a$$

128. Density of unit cell

$$d = \frac{Z \times M}{N_A \times a^3}$$

where,

Z = number of atoms per unit cell

M = molar mass

a^3 = volume of unit cell

[a = edge length]

N_A = Avogadro's number $= 6.022 \times 10^{23}$

For bcc, $Z = 2$, radius $(r) = \frac{\sqrt{3}a}{4}$

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

For fcc, $Z = 4$, $r = \frac{a}{2\sqrt{2}}$

$$\Rightarrow \quad a = 2\sqrt{2}\,r$$

According to question,

$$\frac{d_{\text{room temp.}}}{d_{900^\circ\text{C}}} = \frac{\left(\frac{ZM}{N_A a^3}\right)_{\text{bcc}}}{\left(\frac{ZM}{N_A a^3}\right)_{\text{fcc}}}$$

On substituting the given values, we get

$$\frac{d_{\text{room temp.}}}{d_{900^\circ\text{C}}} = \frac{2 \times M}{N_A \times \left(\frac{4r}{\sqrt{3}}\right)^3} \Bigg/ \frac{4 \times M}{N_A \times (2\sqrt{2}r)^3}$$

[∵ Given, M and r of iron remains constant with temperature]

$$= \frac{2 \times 3\sqrt{3}}{64r^3} \times \frac{16\sqrt{2}r^3}{4}$$

$$\frac{d_{\text{bcc}}}{d_{\text{fcc}}} = \frac{3}{4}\sqrt{\frac{3}{2}}$$

129. Given, Li has a bcc structure.

Density $(\rho) = 530\text{ kg m}^{-3}$

Atomic mass $(M) = 6.94\text{ g mol}^{-1}$

Avogadro's number $(N_A) = 6.02 \times 10^{23}\text{ mol}^{-1}$

We know that, number of atoms per unit cell in bcc $(Z) = 2$.

∴ We have the formula for density,

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

where, a = edge length of a unit cell.

$$\text{or } a = \sqrt[3]{\frac{ZM}{\rho N_A}}$$

$$= \sqrt[3]{\frac{2 \times 6.94\text{ g mol}^{-1}}{0.53\text{ g cm}^{-3} \times 6.02 \times 10^{23}\text{ mol}^{-1}}}$$

$$= \sqrt[3]{4.35 \times 10^{-23}\text{ cm}^{-3}}$$

$$= 3.52 \times 10^{-8}\text{ cm}$$

a = 352 pm

130. Given, ionic radius of cation (A^+)

$$= 0.98 \times 10^{-10}\text{ m}$$

Ionic radius of anion (B^-)

$$= 1.81 \times 10^{-10}\text{ m}$$

$\therefore$ Coordination number of each ion in $AB = ?$

Now, we have

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}}$$

$$= \frac{0.98 \times 10^{-10}\text{ m}}{1.81 \times 10^{-10}\text{ m}} = 0.541$$

If radius ratio range is in between 0.441 – 0.732, ion would have octahedral structure with coordination number 'six'.

131. (a) $FeO_{0.98}$ has non-stoichiometric metal excess defect. It occurs due to missing of a negative ion from its lattice site, thus leaving a hole which is occupied by an electron. Non-stoichiometric ferrous oxide is $FeO_{0.93-0.96}$ and it is due to metal deficiency defect. Thus, statement (a) is incorrect.

(b) In an ionic crystal of A^+B^- type, if equal number of cations and anions are missing from their lattice sites, the defect is called Schottky defect. Due to such defect, density of solid decreases. Thus, statement (b) is correct.

(c) NaCl-insulator; Silicon (Si) - semiconductor, Silver (Ag) - conductor; Quartz - piezoelectric crystal.

Thus, statement (c) is correct.

(d) In an ionic crystal when an ion is missing from its lattice site and occupies interstitial site, the defect is called Frenkel defect. This type of defect is seen in those crystals where the difference in the size of cations and anions is very large and their coordination number is low. Thus, statement (d) is incorrect.

132. Doping of NaCl with 10^{-4} mol% of $SrCl_2$ means, 100 moles of NaCl are doped with 10^{-4} moles of $SrCl_2$.

$\therefore$ 1 mole of NaCl is doped with

$$SrCl_2 = \frac{10^{-4}}{100} = 10^{-6}\text{ mol}$$

As each Sr^{2+} ion introduces one cation vacancy.

$\therefore$ Concentration of cation vacancies

$$= 10^{-6}\text{mol/mol of NaCl}$$
$$= 10^{-6} \times 6.023 \times 10^{23}\text{ mol}^{-1}$$
$$= 6.023 \times 10^{17}\text{ mol}^{-1}$$

16. *Solutions*

133. Total vapour pressure of mixture

= Vapour pressure of pentane in mixture + Vapour pressure of hexane in mixture

Since, the ratio of pentane to hexane = 1 : 4

$\therefore$ Mole fraction of pentane $= \frac{1}{5}$

Mole fraction of hexane $= \frac{4}{5}$

= (mole fraction of pentane × vapour pressure of pentane) + (mole fraction of hexane × vapour pressure of hexane)

$$= \left(\frac{1}{5} \times 440 + \frac{4}{5} \times 120\right)$$

$= (88 + 96) = 184$ mm

$\because$ Vapour pressure of pentane in mixture

= Vapour pressure of mixture × mole fraction of pentane in vapour phase

88 = 184 × mole fraction of pentane in vapour phase

$\therefore$ Mole fraction of pentane in vapour phase

$$= \frac{88}{184} = 0.478$$

134. For a dilute solution, the depression in freezing point (ΔT_f) is directly proportional to molality (m) of the solution.

$$\Delta T_f \propto m \quad \text{or} \quad \Delta T_f = K_f m$$

Where, K_f is called molal depression constant or freezing point depression constant or cryoscopic constant. The value of K_f depends only on nature of the solvent and independent of composition of solute particles, i.e. does not depend on the concentration of solution.

135. Molarity

$$= \frac{\text{Number of moles of solute}}{\text{Volume of solution (in mL)}} \times 1000$$

$$= \frac{25.3 \times 1000}{106 \times 250} = 0.9547 \approx 0.955\text{ M}$$

Na_2CO_3 in aqueous solution remains dissociated as :

$$\underset{x}{Na_2CO_3} \rightleftharpoons \underset{2x}{2Na^+} + \underset{x}{CO_3^{2-}}$$

Since, the molarity of Na_2CO_3 is 0.955 M, the molarity of CO_3^{2-} is also 0.955 M and that of Na^+ is 2×0.955 = 1.910 M

136. Vapour pressure depends upon the surface area of the solution. Larger the surface area, higher is the vapour pressure.

Addition of solute decreases the vapour pressure as some sites of the surface are occupied by solute particles, result in decreased surface area. However, addition of solvent, i.e. dilution, increases the surface area of the liquid surface, thus results in increased vapour pressure.

Hence, addition of water to the aqueous solution of (1 molal) KI, results in increased vapour pressure.

137. Since, component having higher vapour pressure will have higher percentage in vapour phase. Benzene has vapour pressure 12.8 kPa which is greater than toluene 3.85 kPa.

Therefore, the vapour will contain a higher percentage of benzene.

138. From Raoult's law of partial pressure,

$$\frac{p_A^\circ - p_S}{p_S} = \frac{n_B}{n_A}$$

$$\Rightarrow \frac{760 - 732}{732} = \frac{W_B \times M_A}{M_B \times W_A}$$

$$\Rightarrow \frac{28}{732} = \frac{6.5 \times 18}{M_B \times 100}$$

$$\Rightarrow M_B = 30.6$$

$$\therefore \Delta T_b = 0.52 \times \frac{6.5 \times 1000}{30.6 \times 100} = 1.10$$

$\therefore$ Boiling point $= 100 + 1.10$

$= 101.1°\text{C} \approx 101°\text{C}$

139. Molality of solution X = molality of solution Y = 0.2 mol/kg

We know that, elevation in the boiling point (ΔT_b) of a solution is proportional to the molal concentration of the solution. i.e.

$$\Delta T_b \propto m$$

or $\Delta T_b = K_b m$

where, m is the molality of the solution and K_b is molal boiling point constant or ebullioscopic constant.

$\therefore$ By elevation in boiling point relation

$$\Delta T_b = iK_b m$$

or $\Delta T_b \propto i$

where, i is van't Hoff factor.

Since, ΔT_b of solution X is greater than ΔT_b of solution Y. (Observed colligative property is greater than normal colligative property).

$\therefore$ i of solution $X > i$ of solution Y.

$\therefore$ Solution X is undergoing dissociation in water.

140. $Al_2(SO_4)_3 \rightleftharpoons 2\,Al^{3+} + 3\,SO_4^{2-}$

Value of van't Hoff's factor $(i) = 5$

(a) $K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$; $(i = 3)$

(b) $K_3[Fe(CN)_6] \rightleftharpoons 3\,K^+ + [Fe(CN)_6]^{3-}$; $(i = 4)$

(c) $Al(NO_3)_3 \rightleftharpoons Al^{3+} + 3\,NO_3^-$; $(i = 4)$

(d) $K_4[Fe(CN)_6] \rightleftharpoons 4\,K^+ + [Fe(CN)_6]^{3-}$; $(i = 5)$

Therefore, $K_4[Fe(CN)_6]$ has same value of i that of $Al_2(SO_4)_3$, i.e. $i = 5$.

141. According to depression in freezing point,

$$\Delta T_f = i \times k_f \cdot m$$

where, k_f = cryoscopic constant

$$\text{or} \qquad i = \frac{\Delta T_f \times W_{\text{solvent}}}{k_f \times n_{\text{solute}} \times 1000}$$

$$= \frac{3.82 \times 45}{1.86 \times \left(\frac{5}{142}\right) \times 1000} = 2.63$$

142. Depression in freezing point,

$$\Delta T_f = k_f \times m$$

where, m = molality

$$= \frac{W_B \times 1000}{M_B \cdot W_A}$$

$$= \frac{68.5 \times 1000}{342 \times 1000} = \frac{68.5}{342}$$

$$\Delta T_f = 1.86 \times \frac{68.5}{342} = 0.372\ °\text{C}$$

$$T_f = T_f^0 - \Delta T_f = 0 - 0.372°\text{C}$$

$$= -\ 0.372°\text{C}$$

143. Given, molality, $(m) = 0.0020$ m

$$\Delta T_f = 0°\text{C} - 0.00732°\text{C}$$

$$= -0.00732°\text{C}$$

$$k_f = -\ 1.86°\text{C}/\text{m}$$

$$\Delta T_f = i \cdot k_f \times m$$

$$i = \frac{\Delta T_f}{k_f \times m}$$

$$= \frac{0.00732}{1.86 \times 0.0020}$$

$$= 1.96 \approx 2$$

Since, the compound is ionic, so number of moles produced is equal to van't Hoff factor, i.

Hence, 2 moles of ions are produced.

$$\underset{1\ \text{mol}}{[Co(NH_3)_5NO_2]Cl} \longrightarrow \underbrace{[Co(NH_3)_5NO_2]^+ + Cl^-}_{2\ \text{ions}}$$

144. 10 g per dm^3 of urea is isotonic with 5% solution of a non-volatile solute. Hence, between these solutions osmosis is not possible, so their molar concentrations are equal to each other.

Thus, molar concentration of urea solution

$$= \frac{10\ \text{g}/\text{dm}^3}{\text{Molecular weight of urea}}$$

$$= \frac{10}{60}\ \text{M} = \frac{1}{6}\ \text{M}$$

Molar concentration of 5% non-volatile solute

$$= \frac{50\ \text{g}/\text{dm}^3}{\text{Molecular weight of non-volatile solute}} = \frac{50}{m}\ \text{M}$$

Both solutions are isotonic to each other, therefore, $\frac{1}{6} = \frac{50}{m}$

or $m = 50 \times 6 = 300\ \text{g mol}^{-1}$

145. $$\chi_P = \frac{3}{3+2} = \frac{3}{5}$$

$$\chi_Q = \frac{2}{3+2} = \frac{2}{5}$$

Total vapour pressure

$$= \frac{3}{2} \times 80 + \frac{2}{5} \times 60° = 48 + 24 = 72\ \text{torr}$$

17. *Electrochemistry*

146. The relation between molar conductivity (λ_m) and electrolytic conductivity (κ) is given as :

$$\lambda_m = \frac{\kappa \times 1000}{M}$$

where, M is molarity of solution.

Given, concentration of solution,

$$M = 0.5\ \text{mol}/\text{dm}^3$$

Electrolytic conductivity,

$\kappa = 5.76 \times 10^{-3}\ \text{S cm}^{-1}$

Temperature, $\quad T = 298$ K

$\therefore$ Molar conductivity,

$$\lambda_m = \frac{\kappa \times 1000}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5}$$

$$= 11.52\ \text{S cm}^2/\text{mol}$$

147. Given, molar conductance at 0.1 M concentration,

$$\lambda_c = 9.54\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Molar conductance at infinite dilution,

$$\lambda_c^{\infty} = 238\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

We know that, degree of ionisation,

$$\alpha = \frac{\lambda_c}{\lambda_c^{\infty}} \times 100$$

$$= \frac{9.54}{238} \times 100 = 4.008\%$$

148. Since, 22400 mL volume is occupied by 1 mole of O_2 at STP.

Thus, 5600 mL O_2 means

$$= \frac{5600}{22400}\ \text{mol}\ O_2 = \frac{1}{4}\ \text{mol}\ O_2$$

$$\therefore \quad \text{Weight of } O_2 = \frac{1}{4} \times 32 = 8\ \text{g}$$

According to problem,

Equivalents of Ag = Equivalents of O_2

$$= \frac{\text{Weight of Ag}}{\text{Equivalent weight of Ag}}$$

$$= \frac{W_{O_2}}{\text{Equivalent weight of } O_2}$$

$$\frac{w_{\text{Ag}}}{M_{\text{Ag}}} = \frac{w_{O_2}}{M_{O_2}}$$

$$\therefore \quad \frac{w_{\text{Ag}}}{108} \times 1 = \frac{8}{32} \times 4$$

$$[\because 2H_2O \longrightarrow O_2 + 4H^+ + 4e^-]$$

$$\Rightarrow \quad w_{\text{Ag}} = 108\ \text{g}$$

149. Al_2O_3 ionises as :

$$Al_2O_3 \rightleftharpoons \underset{\text{Cathode}}{Al^{3+}} + \underset{\text{Anode}}{AlO_3^{3-}}$$

At cathode

$$\underset{3\text{F}}{Al^{3+} + 3e^-} \longrightarrow \underset{27\,\text{g}}{Al}$$

$\because$ Mass of aluminium deposited by 3 F of electricity = 27

$\therefore$ Mass of aluminium deposited by $4.0 \times 10^4 \times 6 \times 3600$ C of electricity

$$= \frac{27 \times 4.0 \times 10^4 \times 6 \times 3600}{3\ \text{F}}\ \text{g}$$

$$= \frac{27 \times 4.0 \times 10^4 \times 6 \times 3600}{3 \times 96500}\ \text{g}$$

$$= 8.1 \times 10^4\ \text{g}$$

150. Anode is always the site of oxidation thus, anode half-cell is

$$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s); \quad E° = -\ 0.76\ \text{V}$$

Cathode half-cell is

$$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq);\ E° = 0.34\ \text{V}$$

$$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}}$$

$$= 0.34 - (-\ 0.76)$$

$$= +\ 1.10\ \text{V}$$

151. Given that $E°_{Fe^{2+}/Fe} = -\ 0.441$ V

So, $Fe \longrightarrow Fe^{2+} + 2e^-$;

$E° = +\ 0.441$ V ...(i)

and $E°_{Fe^{3+}/Fe^{2+}} = 0.771$ V

So, $2\,Fe^{3+} + 2e^- \longrightarrow 2\,Fe^{2+}$;

$$E^\circ = 0.771\text{ V} \quad \ldots\text{(ii)}$$

Cell reaction

$$\begin{array}{l}
\text{(i) } Fe \longrightarrow Fe^{2+} + 2e^-, \quad E^\circ = 0.441\text{ V} \\
\text{(ii) } 2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}, \\
\qquad\qquad E^\circ = +\,0.771\text{ V} \\
\hline
Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}, \\
\qquad\qquad E^\circ_{cell} = 1.212\text{ V} \\
\hline
\end{array}$$

Alternative On the basis of cell reaction following half-cell reactions are written.

At anode

$Fe \longrightarrow Fe^{2+} + 2e^-$ (oxidation)

At cathode

$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ (reduction)

$$\begin{aligned}
\text{So, } E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\
&= (+\,0.771) - (-\,0.441) \\
&= +\,1.212\text{ V.}
\end{aligned}$$

152 The reaction in which same species is oxidised as well as reduced is called disproportionation reaction. Firstly, calculate the value of E°_{cell} of each species undergoing disproportionation reaction. The reaction whose E°_{cell} value is positive will be feasible (spontaneous).

(i) Given, $BrO_3^- \longrightarrow HBrO$;

$$E^\circ_{BrO_3^-/HBrO} = 1.5\text{ V}$$

$$BrO_3^- \longrightarrow BrO_4^-;$$

$$E^\circ_{BrO_3^-/BrO_4^-} = -1.82\text{ V}$$

$$\therefore \quad 2\overset{+5}{Br}O_3^- \longrightarrow H\overset{+1}{Br}O + \overset{+7}{Br}O_4^-$$

$$\begin{aligned}
E^\circ_{cell} &= E^\circ_{red} + E^\circ_{ox} \\
&= E^\circ_{BrO_3^-/HBrO} + E^\circ_{BrO_3^-/BrO_4^-} \\
&= 1.5 - 1.82 = -0.32\text{ V} \\
&\qquad\qquad \text{[Non-spontaneous]}
\end{aligned}$$

(ii) $H\overset{+1}{Br}O \longrightarrow \overset{0}{Br_2}$;

$$E^\circ_{HBrO/Br_2} = 1.595\text{ V}$$

$$H\overset{+1}{Br}O \longrightarrow \overset{+5}{Br}O_3^-;$$

$$E^\circ_{HBrO/BrO_3^-} = -1.5\text{ V}$$

$$2H\overset{+1}{Br}O \longrightarrow \overset{0}{Br_2} + \overset{+5}{Br}O_3^-$$

$$\begin{aligned}
E^\circ_{cell} &= E^\circ_{HBrO/Br_2} + E^\circ_{HBrO/BrO_3^-} \\
&= 1.595 - 1.5 \\
&= 0.095\text{ V} \qquad \text{[Spontaneous]}
\end{aligned}$$

(iii) $\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-}$; $E^\circ_{Br_2/Br^-} = 1.0652\text{ V}$

$$\overset{0}{Br_2} \longrightarrow H\overset{+1}{Br}O\,;\ E^\circ_{Br_2/HBrO} = -1.595\text{ V}$$

$$2\overset{0}{Br_2} \longrightarrow \overset{-1}{Br^-} + H\overset{+1}{Br}O$$

$$\begin{aligned}
E^\circ_{cell} &= E^\circ_{Br_2/Br^-} + E^\circ_{Br_2/HBrO} \\
&= 1.0652 - 1.595 \\
&= -0.5298\text{ V} \\
&\qquad\qquad \text{(Non-spontaneous)}
\end{aligned}$$

Among the given options, only HBrO undergoes disproportionation.

153. Calculate the value of E_{cell}, i.e. E_1 and E_2 by substituting the respective given values in the Nernst equation,

$$E_{cell} = E^\circ - \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Compare the calculated values of E_1 and E_2 and find the correct relation.

For the electrochemical cells,

$Zn|ZnSO_4(0.01M)||CuSO_4(1M)|Cu$

Cell reaction :

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu;\ n = 2$$

$$\begin{aligned}
E_1 &= E^\circ - \frac{0.059}{2}\log\frac{Zn^{2+}}{Cu^{2+}} \\
&= E^\circ - \frac{0.059}{2}\log\frac{0.01}{1} \\
E_1 &= E^\circ - \frac{0.059}{2}\log\frac{1}{100} \\
&= (E^\circ + 0.059)
\end{aligned}$$

For cell,

$Zn|ZnSO_4(1M)||CuSO_4(0.01M)|Cu$

$$E_2 = E^\circ - \frac{0.059}{2}\log\frac{1}{0.01}$$

$$E_2 = E^\circ - \frac{0.059}{2}\log 100 = (E^\circ - 0.059)$$

$$\Rightarrow \quad E_1 > E_2$$

154. From the question, we have an equation

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

According to Nernst equation,

$$\begin{aligned}
E &= E^\circ - \frac{0.0591}{2}\log\frac{p_{H_2}}{[H^+]^2} \\
&= 0 - \frac{0.0591}{2}\log\frac{p_{H_2}}{(10^{-7})^2} \\
&\qquad\qquad [\because (H^+) = 10^{-7}]
\end{aligned}$$

$\therefore$ For potential of H_2 electrode to be zero, p_{H_2} should be equal to $[H^+]^2$, i.e. 10^{-14} atm.

$$\therefore \quad \log\frac{10^{-14}}{(10^{-7})^2} = 0$$

155. We know that, standard Gibbs energy,

$$\Delta G^\circ = -\,nFE^\circ_{cell}$$

For the cell reaction,

$$2\,Ag^+ + Cu \longrightarrow Cu^{2+} + 2\,Ag;$$

$$E^\circ_{cell} = +\,0.46\text{ V}$$

$$\begin{aligned}
\Delta G^\circ &= -\,nFE^\circ_{cell} \\
n &= 2 \\
\Delta G^\circ &= -\,2 \times 96500 \times 0.46 \\
&= -\,88780\text{ J} \\
&= -\,88.7\text{ kJ} \approx -\,89.0\text{ kJ}
\end{aligned}$$

156. ΔG of $H_2O(l) = -\,237.2$ kJ / mol

ΔG of $CO_2(g) = -\,394.4$ kJ / mol

ΔG of pentane $(g) = -\,8.2$ kJ / mol

In pentane-oxygen fuel cell following reaction takes place.

$$\begin{array}{l}
C_5H_{12} + 10H_2O(l) \longrightarrow 5CO_2 \\
\qquad\qquad\qquad + 32\,H^+ + 32e^- \\
8O_2 + 32H^+ + 32e^- \longrightarrow 16\,H_2O(l) \\
\hline
C_5H_{12} + 8O_2 \longrightarrow 5CO_2 + 6H_2O(l), \\
\qquad\qquad\qquad E^\circ = ?
\end{array}$$

$$\begin{aligned}
\Delta G_{reaction} &= \Sigma\Delta G_{product} - \Sigma\,\Delta G_{reactant} \\
&= 5 \times \Delta G_{(CO_2)} + 6\Delta G_{(H_2O)} \\
&\qquad - [\Delta G_{(C_5H_{12})} + 8 \times \Delta G_{O_2}] \\
&= 5 \times (-394.4) + 6 \times (-237.2) \\
&\qquad -(-8.2 + 0) \\
&= -\,1972 - 1423.2 + 8.2 \\
&= -\,3387\text{ kJ / mol} \\
&= -3387 \times 10^3\text{ J / mol}
\end{aligned}$$

$$\Delta G = -\,nFE^\circ_{cell}$$

$$-3387 \times 10^3 = -\,32 \times 96500 \times E^\circ_{cell}$$

$$E^\circ_{cell} = \frac{-3387 \times 10^3}{-\,32 \times 96500} = 1.0968\text{ V}$$

157. By Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{2.303\,RT}{nF}\log_{10}K$$

At equilibrium, $E_{cell} = 0$

Given that, $R = 8.314\text{ JK}^{-1}\text{ mol}^{-1}$

$T = 25°\text{C} + 273 = 298$ K

$F = 96500$ C and $n = 2$

$$\begin{aligned}
\therefore E^\circ_{cell} &= \frac{2.303 \times 8.314 \times 298}{2 \times 96500}\log_{10}K \\
&= \frac{0.0591}{2}\log_{10}K
\end{aligned}$$

Given that $E^\circ_{cell} = 0.295$ V

$$\therefore \quad 0.295 = \frac{0.0591}{2}\log_{10}K$$

$$\log_{10}K = \frac{0.295 \times 2}{0.0591} = 10$$

$$\text{antilog}\log_{10}K = \text{antilog } 10$$

$$\text{and} \qquad K = 1 \times 10^{10}$$

18. *Chemical Kinetics*

158. For the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\begin{aligned}
\text{Rate} &= -\frac{d\,[N_2]}{dt} = -\frac{1}{3}\frac{d\,[H_2]}{dt} \\
&= +\frac{1}{2}\frac{d\,[NH_3]}{dt}
\end{aligned}$$

$$\text{or} -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$-\frac{d[H_2]}{dt} = \frac{3}{2} \times 2 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

$$= 3 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

159. For the reaction,

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The rate of reaction w.r.t.

$$N_2 = -\frac{d[N_2]}{dt}$$

[Rate of disappearance]

The rate of reaction with respect to

$$H_2 = -\frac{1}{3}\frac{d[H_2]}{dt}$$

[Rate of disappearance]

The rate of reaction with respect to

$$NH_3 = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

[Rate of appearance]

Hence, at a fixed time

$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$\text{or } +\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$$

$$\text{or } +\frac{d[NH_3]}{dt} = -\frac{2d[N_2]}{dt}$$

160. For the reaction,

$A + B \longrightarrow$ Products

On doubling the initial concentration of A only, the rate of the reaction is also doubled, therefore

$$\text{Rate} \propto [A]^1 \quad \ldots\text{(i)}$$

Let initial rate law is

$$\text{Rate} = k[A][B]^y \quad \ldots\text{(ii)}$$

If concentration of A and B both are doubled, the rate gets changed by a factor of 8.

$$8 \times \text{rate} = k[2A][2B]^y \quad \ldots\text{(iii)}$$

$$[\because \text{Rate} \propto [A]^1]$$

Dividing Eq. (iii) by Eq. (ii), we get

$$8 = 2 \times 2^y$$

$$4 = 2^y$$

$$(2)^2 = (2)^y$$

$$\therefore \quad y = 2$$

Hence, rate law is, rate $= k[A][B]^2$

161. We know that, slowest step is the rate determining step.

$$\therefore \quad \text{Rate } (r) = K_1[X][Y_2] \quad \ldots\text{(i)}$$

Now, from equation (i), i.e.

$$X_2 \rightarrow 2X \text{ [fast]}$$

$$K_{eq} = \frac{[X]^2}{[X_2]}$$

$$[X] = \{K_{eq}[X_2]\}^{1/2} \quad \ldots\text{(ii)}$$

Now, substitute the value of $[X]$ from equation (ii) in equation (i), we get

$$\text{Rate } (r) = K_1(K_{eq})^{1/2}[X_2]^{1/2}[Y_2]$$

$$= K[X_2]^{1/2}[Y_2]$$

$$\therefore \text{Order of reaction} = \frac{1}{2} + 1 = \frac{3}{2} = 1.5$$

162. $A + B \longrightarrow$ Product

$$\text{Rate, } r \propto [A]^x [B]^y \quad \ldots\text{(i)}$$

The rate decreases by a factor 4 if the concentration of reactant B is doubled.

$$\frac{r}{4} \propto [A]^x[2B]^y \quad \ldots\text{(ii)}$$

From Eqs. (i) and (ii)

$$4 = \left(\frac{1}{2}\right)^y \text{ and } y = -2$$

Hence, order of reaction with respect to B is –2.

163. For a first order reaction,

$$\text{Rate constant } (k) = \frac{2.303}{t}\log\frac{a}{a-x}$$

where, a = initial concentration

$a - x$ = concentration after time 't'

t = time in sec.

Given, $a = 20$ g, $a - x = 5$ g,

$k = 10^{-2}$

$$\therefore \quad t = \frac{2.303}{10^{-2}}\log\frac{20}{5}$$

$$= 138.6 \text{ s}$$

Alternatively,

Half-life for the first order reaction,

$$\frac{t_{1/2}}{2} = \frac{0.693}{k} = \frac{0.693}{10^{-2}} = 69.3 \text{ s}$$

Two half-lives are required for the reduction of 20 g of reactant into 5 g.

$$20 \text{ g} \xrightarrow{t_{1/2}} 10 \text{ g} \xrightarrow{t_{1/2}} 5 \text{ g}$$

$\therefore$ Total time

$$= 2t_{1/2} = 2 \times 69.3 = 138.6 \text{ s}$$

164. For first order reaction,

$$A \longrightarrow B$$

$$\text{Rate} = k \times [A]$$

$$\text{Rate} = 2.0 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

$$[A] = 0.01 \text{ M}$$

$$\text{So, } 2.0 \times 10^{-5} = k \times 0.01$$

$$k = \frac{2.0 \times 10^{-5}}{0.01} \text{ s}^{-1}$$

$$= 2.0 \times 10^{-3} \text{ s}^{-1}$$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.0 \times 10^{-3}}$$

$$= 346.5 \approx 347 \text{ s}$$

165. For first order reactions, the rate of reaction is proportional to the first power of the concentration of the reactant .

For, $A \rightarrow B$

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]$$

[where, k = constant]

$$\text{Half-life } (t_{1/2}) = \frac{0.693}{k}$$

$\therefore$ Rate of first order reaction depends upon reactant concentrations and half-life does not depend upon initial concentration of reactant, $[A]_0$.

For second order reactions, the rate of reaction is proportional to the second power of the concentration of the reactant.

For, $2A \rightarrow B$

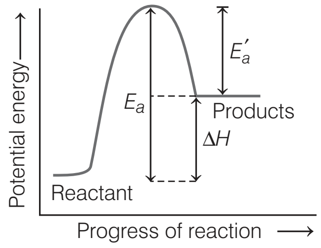
$$\text{Rate} = k[A]^2$$

$$\text{Half-life } (t_{1/2}) = \frac{1}{k[A]_0}$$

$\therefore$ Rate of second order reaction depends upon reactant concentration and half-life also does depend on $[A]_0$.

166. In endothermic reactions, energy of reactants is less than that of the products.

Potential energy diagram for endothermic reactions is



where,

E_a = activation energy of forward reaction

E'_a = activation energy of backward reaction

ΔH = enthalpy of the reaction.

From the above diagram,

$$E_a = E'_a + \Delta H$$

$$\text{Thus,} \quad E_a > \Delta H$$

167. By Arrhenius equation

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

where, E_a = energy of activation

Applying log on both the side,

$$k = \frac{2.303}{t}\log\frac{A_t}{A_0} = \frac{2.303}{105}\log\frac{0.04}{0.03}$$

$$= \frac{2.303}{105} \times 0.124$$

$$k = 0.028 \text{ s}^{-1}$$

We know that,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.028 \text{ s}^{-1}}$$

$$= 24.14 \text{ s} \approx 24.1 \text{ s}$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \ldots(i)$$

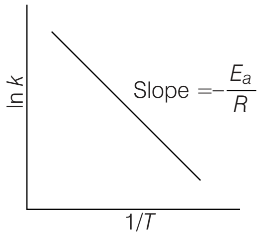
or $$\log k = -\frac{E_a}{2.303RT} + \log A \qquad \ldots(ii)$$

Compare the above equation w.r.t. straight line equation of $y = mx + c$.

Thus, if a plot of $\ln k$ vs $\frac{1}{T}$ is a straight line, the validity of the equation is confirmed.

Slope of the line $= -\frac{E_a}{R}$

Thus, measuring the slope of the line, the value of E_a can be calculated.



168. Given, $k_1 = 10^{16} \cdot e^{-2000/T}$ and $k_2 = 10^{15} \cdot e^{-1000/T}$

On taking log of both the equations we get

$$\log k_1 = 16 - \frac{2000}{2.303T}$$

and $$\log k_2 = 15 - \frac{1000}{2.303T}$$

At $k_1 = k_2$

$$16 - \frac{2000}{2.303T} = 15 - \frac{1000}{2.303T}$$

$$\Rightarrow \quad T = \frac{1000}{2.303}\text{ K}$$

169. Given, initial temperature,

$$T_1 = 20 + 273 = 293\text{ K}$$

Final temperature,

$$T_2 = 35 + 273 = 308\text{ K}$$
$$R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$$

Since, rate becomes double on raising temperature,

$$\therefore \quad r_2 = 2r_1 \quad \text{or} \quad \frac{r_2}{r_1} = 2$$

As rate constant, $k \propto r$

$$\therefore \quad \frac{k_2}{k_1} = 2$$

From Arrhenius equation, we know that

$$\log \frac{k_2}{k_1} = -\frac{E_a}{2.303\,R}\left[\frac{T_1 - T_2}{T_1T_2}\right]$$

$$\log 2 = -\frac{E_a}{2.303 \times 8.314}\left[\frac{293 - 308}{293 \times 308}\right]$$

$$0.3010 = -\frac{E_a}{2.303 \times 8.314}\left[\frac{-15}{293 \times 308}\right]$$

$$\therefore E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 293 \times 308}{15}$$

$$= 34673.48\text{ J mol}^{-1}$$
$$= 34.7\text{ kJ mol}^{-1}$$

19. *Surface Chemistry*

170. ΔS [change in entropy] and ΔH [change in enthalpy] are related by the equation

$$\Delta G = \Delta H - T\Delta S$$

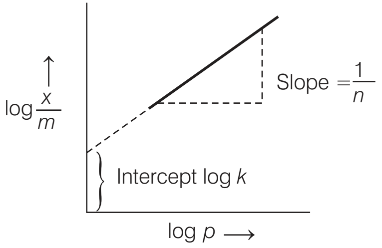
[Here, ΔG = change in Gibbs free energy]

For adsorption of a gas, ΔS is negative because randomness decreases. Thus, in order to make ΔG negative [for spontaneous reaction], ΔH must be highly negative because reaction is exothermic. Hence, for the adsorption of a gas, if ΔS is negative, therefore, ΔH should be highly negative.

171. $\frac{x}{m} = p \times T$ is the incorrect relation.

The correct relation is amount of adsorption $\frac{x}{m} \propto \frac{p}{T}$.

172. If we plot a graph between $\log\left(\frac{x}{m}\right)$ and $\log p$, a straight line will be obtained. The slope of the line is equal to $\frac{1}{n}$ and the intercept is equal to $\log k$.



where, $\frac{x}{m}$ = amount of adsorption

According to Freundlich adsorption isotherm

$$\frac{x}{m} = Kp^{1/n}$$

Taking log of both sides,

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

from $\quad y = zx + c$

$$z = \frac{1}{n}\text{ (slope)}$$

173. The main points of Langmuir's theory of adsorption are as :

(i) Adsorption takes place on the surface of the solid only till the whole of the surface is completely covered with a unimolecular layer of the adsorbed gas, i.e. the adsorption sites are equivalent in their ability to absorb the particles.

(ii) Adsorption consist of two opposing processes (a) condensation and (b) evaporation.

(iii) The rate of condensation depend upon the uncovered surface of the adsorbent available for condensation.

174. Most of the enzymes have proteinous nature. They are highly specific and get denaturated by high temperature or UV-rays. At optimum temperature, which is generally in between 15°-25°C, enzyme activity is maximum.

175. **Coagulation** is generally brought about by the addition of electrolytes. When an electrolyte is added to a colloidal solution, the particles of the sol take up the ions which are oppositely charged. As a result, their charge gets neutralised.

Electrophoresis The movement of colloidal particles under an applied electric potential is called electrophoresis.

Electroosmosis may be defined as a phenomenon in which the molecules of the dispersion medium are allowed to move under the influence of an electric field whereas colloidal particles are not allowed to move.

Tyndall effect is the scattering of light by sol particles, which cannot be affected by charge on them.

176. The process of settling of colloidal particles due to the neutralisation of their charge by any means is called coagulation.

Coagulation power of an ion depends both on magnitude and sign of the charge (positive or negative) on the ion. This fact can be explained by **Hardy-Schulze rule.**

According to this rule "greater the valency of the coagulating ion/flocculating ion (oppositely charged ion) added, the greater is its power to cause coagulation.

To coagulate a positively charged sol, the order of coagulating power of negative ion is

$$I^- < SO_4^{2-} < PO_4^{3-} < [Fe(CN)_6]^{4-}.$$

Similarly, to coagulate a negatively charged sol, the order of coagulating power of positive ions is

$$Ag^+ < Pb^{2+} < Fe^{3+} < Si^{4+}.$$

177. Lower the coagulating power, higher is the coagulation value in millimoles per litre, i.e. coagulating power is inversely proportional to coagulation value. Thus, correct order of their coagulating power is

$MgSO_4 > BaCl_2 > NaCl$ or III > II > I

20. *General Principles and Process of Isolation of Elements*

178. Galena (PbS), copper pyrites ($CuFeS_2$) and argentite (Ag_2S) are concentrated by froth floatation process but sphalerite (ZnS) is concentrated by chemical leaching.

179. Carbon and hydrogen are not suitable reducing agents for metal sulphides.

180. SO_2 gas is obtained when any sulphide ore is roasted.

$$2M_2S + 3\,O_2 \xrightarrow{\Delta} 2M_2O + 2\,SO_2$$

This gas exhibits all the characteristics that are given in the question.

181. Extraction of gold and silver involves leaching with CN^-ion. Silver is later recovered by displacement of Zn.

In the metallurgy of silver or gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air to obtain the metal in solution as complex. From the complex, metal is obtained later by replacement.

In general,

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \longrightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$$

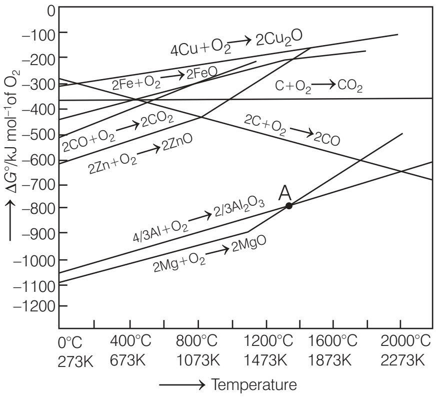
$$2[M(CN)_2]^-(aq) + Zn(s) \longrightarrow [Zn(CN)_4]^{2-}(aq) + 2M(s)\,;\quad M = \text{Ag or Au}$$

This method is known as **Mac-Arthur** forest cyanide process.

182. Ellingham diagrams help us in predicting the feasibility of thermal reduction of an ore. The criterion of feasibility is that at a given temperature, Gibbs energy of the reaction must be negative.

According to Ellingham diagram, the temperature at which two lines intersect shows that the metal will reduce the oxide of other metals which lie above it in Ellingham diagram.

In other words, the metal oxide having more negative value of ΔG_f° can reduce the oxide having less negative ΔG_f°. As, Mg has more $-\Delta G^\circ$ value than alumina, so it will be in lower part of Ellingham diagram. Hence, Mg will be used to reduce alumina.



Gibbs energy ΔG° *vs* T plots (schematic) for formation of some oxides (Ellingham diagram).

183. Alumina, Al_2O_3 is a bad conductor of electricity and has very high melting point, so before subjecting to electrolysis, it is mixed with fluorspar (CaF_2) and cryolite (Na_3AlF_6), which lower its melting point and make it more conducting. Mainly CaF_2 and Na_3AlF_6 are mixed with Al_2O_3 for converting Al_2O_3in molten state.

184. In the extraction of copper from its sulphide ore, when ore is subjected to roasting, some of it is oxidised to Cu_2O which reacts with the remaining Cu_2S (sulphide ore) to give copper metal.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2 \uparrow$$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2 \uparrow$$

In this process Cu_2S behaves as reducing agent.

185. A → 4, B → 2, C → 3, D → 1

Cyanide process It is a metallurgical technique for extracting Au (gold) from low grade ore by converting the Au to a water-soluble coordination complex.

Froth floatation process This process is used for dressing of sulphide ore, i.e. ZnS.

Electrolytic reduction This process is used for extraction of Al which is carried out in a steel tank lined inside with graphite. Here, graphite serves as cathode. The electrolyte consists of alumina dissolved in fused cryolite (Na_3AlF_6) and fluorspar (CaF_2).

Zone refining This process is used for ultra pure Ge element. An ingot of Ge is first purified by zone refining. Then a small amount of antimony is placed in the molten zone which is passed through the pure Ge with the proper choice of rate of heating and other variables.

21. *p-block Elements*

186. Let the oxidation state of nitrogen in each of the given N-compounds be x.

(i) $HNO_3 : +1 + x + 3(-2) = 0$

$$x = +5$$

∴ Oxidation state of N in HNO_3 is +5.

(ii) $NO : x + 1(-2) = 0$

$$x = +2$$

∴ Oxidation state of N in NO is +2.

(iii) $NH_4Cl : x + 4(+1) + 1(-1) = 0$

$$x = -3$$

∴ Oxidation state of N in NH_4Cl is –3.

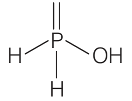
(iv) $N_2 : x = 0$ [∵ N_2 is present in elemental state]

∴ Oxidation state of N in N_2 is 0.

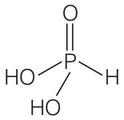
Thus, the correct decreasing order of oxidation states of given N- compounds will be

$$H\overset{+5}{N}O_3 > \overset{+2}{N}O > \overset{0}{N_2} > \overset{-3}{N}H_4Cl$$

187. Phosphinic acid

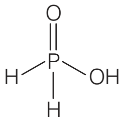


Phosphonic acid



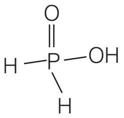
Due to the presence of one replaceable proton in phosphinic acid, it is monoprotic acid. And due to presence of two replaceable proton in phosphonic acid, it is diprotic acid.

188. The oxy acid of phosphorus which contain P—H bond act as a reducing agent or reductant.



In H_3PO_2 one —OH group and two P—H bonds are present.

189. Hypophosphorus acid, H_3PO_2, has the following structure.



As it contains only one replaceable H-atom (that is attached with O, not with P directly) so, it is a monoprotic acid.

All other given statements are true.

190. Since, electron repulsion predominate over the stability gained by achieving noble gas configuration. Hence, formation of O^{2-} in gas phase is unfavourable.

191. $S_4O_6^{2-}$ and $S_2O_3^{2-}$ have S—S bond

192. An oxidising agent is a species, which oxidises the other species and itself gets reduced.

(i) $C\overset{0}{u} + 2H_2SO_4 \longrightarrow \overset{+2}{Cu}SO_4 + SO_2 + 2H_2O$

(ii) $3\overset{0}{S} + 2H_2SO_4 \longrightarrow 3\overset{+4}{S}O_2 + 2H_2O$

(iii) $\overset{0}{C} + H_2SO_4 \longrightarrow \overset{+4}{C}O_2 + 2SO_2 + 2H_2O$

(iv) $\overset{+2}{Ca}\overset{-1}{F_2} + H_2SO_4 \longrightarrow \overset{+2}{Ca}SO_4 + 2H\overset{-1}{F}$

In reaction (iv), oxidation number of elements remains unchanged. Thus, in this reaction, H_2SO_4 does not act as an oxidising agent.

193. (a) Fluorine is the most electronegative element and cannot exhibit any positive oxidation state. Other halogens have *d*-orbitals and therefore, can expand their octets and show +1, +3, +5 and +7 oxidation states. Thus, option (a) is incorrect.

Fluorine can form an oxoacid, HOF in which oxidation state of F is +1. But HOF is highly unstable compound.

(b) All halogens are strong oxidising agents as they have strong tendency to accept an electron. Thus, option (b) is correct.

(c) All halogens form monobasic oxyacids. Thus, option (c) is also correct.

(d) Electron gain enthalpy of halogens become less negative down the group. However, the negative electron gain enthalpy of fluorine is less than chlorine due to small size of fluorine atom.

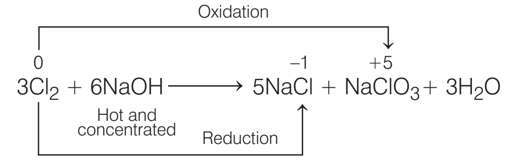
Thus, option (d) is also correct.

194. Incorrect order of bond dissociation energy $F_2 > Cl_2 > Br_2 > I_2$ due to following order of size I> Br> Cl> F.

195. Since, there is a strong hydrogen bonding between HF molecules. Hence, boiling point is highest for HF.

HF > HI > HBr > HI

196. When chlorine gas reacts with hot and concentrated NaOH solution, it disproportionates into chloride (Cl^-) and chlorate (ClO_3^-) ions.



$$3\overset{0}{Cl_2} + 6NaOH \xrightarrow[\text{concentrated}]{\text{Hot and}} 5Na\overset{-1}{Cl} + Na\overset{+5}{Cl}O_3 + 3H_2O$$

In this process, oxidation number of chlorine changes from 0 to −1 and 0 to +5.

Note *In disproportionation reactions, the same element undergoes oxidation as well as reduction.*

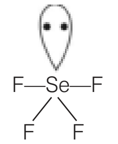
197. Two different halogens may react to form interhalogen compounds as :

A. *XX′* (ClF, BrF, BrCl, IF, ICl) → Linear
B. *XX′*$_3$ (ClF_3, BrF_3, IF_3, ICl_3) → Bent T-shaped
C. *XX′*$_5$ (ClF_5, $BrCl_5$, IF_5) → Square-pyramidal
D. *XX′*$_7$ (IF_7) → Pentagonal bipyramidal

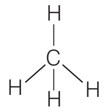
198. PH_5 does not exist due to very less electronegativity difference between P and H. Hydrogen is slightly more electronegative than phosphorus, thus could not hold significantly the sharing electrons.

On the other hand, $BiCl_5$ does not exist due to inert pair effect. On moving down the group, +5 oxidation state becomes less stable while +3 oxidation state becomes more stable.

In SO_2, $p\pi$-$d\pi$ and $p\pi$-$p\pi$ both types of bonds are present.

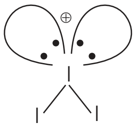


See-saw shape



Tetrahedral

Thus, SeF_4 and CH_4 do not have same shape.

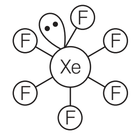


Geometry-Bent

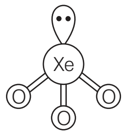
Thus, option (c) is incorrect statement.

199. A → 1, B → 3, C → 4, D → 2

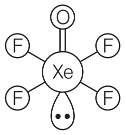
The structure of the xenon compounds are represented below:



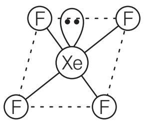
Distorted octahedral (XeF_6)



Pyramidal (XeO_3)



Square pyramidal ($XeOF_4$)



Square planar (XeF_4)

22. *d and f-block Elements*

200. In $_{23}V = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^2$

Third electron which is removed to give third ionisation potential, belongs to $3d^3$-subshell.

$_{24}Cr = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^1$

Third electron which is removed to give third ionisation potential, belongs to $3d^5$-subshell.

$_{26}Fe = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6, 4s^2$

Third electron which is removed to give third ionisation potential, belongs to $3d^6$-subshell.

$_{25}Mn = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$

Third electron which is removed to give third ionisation potential, belongs to $3d^5$-subshell.

In all elements shell and subshells are same. Required amount of energy (enthalpy) is based upon the stability of d-subshell.

The $3d^5$-subshell has highest stability in all because it is half-filled subshell. So, Mn shows highest third ionisation potential.

201. Spin magnetic moment can be calculated as :

$$\mu = \sqrt{n(n+2)}\ \text{BM}$$

where, μ = magnetic moment

BM = Bohr Magneton (unit of μ)

n = number of unpaired electrons in d-orbital.

The electronic configuration of Co^{3+} is $[Ar]\ 3d^6$.

Here, $n = 4$

$$\mu = \sqrt{4(4+2)} = \sqrt{24}\ \text{BM}$$

The electronic configuration of Cr^{3+} is $[Ar]\ 3d^3$.

Here, $n = 3$

$$\mu = \sqrt{3(3+2)} = \sqrt{15}\ \text{BM}$$

The electronic configuration of Fe^{3+} is $[Ar]\ 3d^5$.

Here, $n = 5$

$$\mu = \sqrt{5(5+2)} = \sqrt{35}\ \text{BM}$$

The electronic configuration of Ni^{2+} is $[Ar]\ 3d^8$.

Here, $n = 2$

$$\mu = \sqrt{2(2+2)} = \sqrt{8}\ \text{BM}$$

So, the correct option is (c).

202. Magnetic moment, $\mu = \sqrt{n(n+2)}$ BM

where,

n = number of unpaired electrons,

$\mu = 2.84$ (given)

$$\therefore \quad 2.84 = \sqrt{n(n+2)}\ \text{BM}$$

$$(2.84)^2 = n(n+2)$$

$$8 = n^2 + 2n$$

$$n^2 + 2n - 8 = 0$$

$$n^2 + 4n - 2n - 8 = 0$$

$$n(n+4) - 2(n+4) = 0$$

$$n = 2$$

$Ni^{2+} = [Ar]\ 3d^8 4s^0$ (two unpaired electrons)

$Ti^{3+} = [Ar]\ 3d^1 4s^0$ (one unpaired electrons)

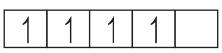
$Cr^{3+} = [Ar]\ 3d^3$ (three unpaired electrons)

$Co^{2+} = [Ar], 3d^7, 4s^0$ (three unpaired electrons)

So, only Ni^{2+} has 2 unpaired electrons.

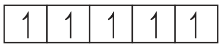
203.

$Cr^{2+} : d^4$



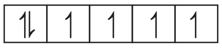
(4 unpaired electrons)

$Mn^{2+} : d^5$



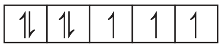
(5 unpaired electrons)

$Fe^{2+} : d^6$



(4 unpaired electrons)

$Co^{2+} : d^7$



(3 unpaired electrons)

$\therefore [Co(H_2O)_6]^{2+}$ has minimum number of unpaired electrons and thus, shows minimum paramagnetic behaviour.

Higher the unpaired e^-.

Higher the magnetic moment

$$\mu = \sqrt{n(n+2)}$$

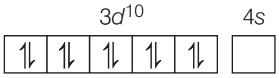
n = number of unpaired e^-

204. In TiF_6^{2-}, Ti is present as Ti^{4+}

$$Ti^{4+} = [Ar]\ 3d^0 4s^0$$

Hence, TiF_6^{2-} is colourless due to the absence of unpaired electrons.

In Cu_2Cl_2, Cu is present as Cu^+.



Due to absence of unpaired electrons, Cu_2Cl_2 is colourless.

205. $HgCl_2$ and I_2 both when dissolved in water containing I^- ions, the pair of species formed is HgI_4^{2-} and I_3^-.

In aqueous solution, I_2 reacts with I^- and maintains the following equilibrium.

$$I_2 + I^- \rightleftharpoons I_3^-$$

Hg^{2+} gives ppt. of HgI_2 on reaction with I^-.

But HgI_2 is soluble in excess of I^-.

$$Hg^{2+} + 2I^- \longrightarrow \underset{\text{Red ppt.}}{HgI_2} \downarrow + 2Cl^-$$

$$HgI_2 + 2I^- \rightleftharpoons [HgI_4]^{2-}$$

206. When SO_2 is passed through acidified $K_2Cr_2O_7$ solution, green chromium sulphate is formed. In this reaction, oxidation state of Cr changes from +6 to +3.

$$\underset{\text{OS of Cr=+6}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 \longrightarrow$$

$$K_2SO_4 + \underset{\substack{\text{OS of Cr= +3}\\\text{(Green)}}}{Cr_2(SO_4)_3} + H_2O$$

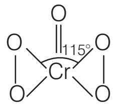
The appearance of green colour is due to the reduction of chromium metal.

207. When H_2O_2 is added to an acidified solution of a dichromate $Cr_2O_7^{2-}$, a deep blue coloured complex, chromic peroxide CrO_5 [or $CrO(O_2)_2$] is formed.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O \longrightarrow \underbrace{2CrO(O_2)_2}_{\text{Chromic peroxide}}$$

$$[\text{blue coloured complex}] + 5H_2O$$

This deep blue coloured complex has the following structure.



Oxidation state of Cr in CrO_5 is +6 due to the presence of two peroxide linkages which can be calculated as

$$\underset{\text{[For Cr]}}{x} + \underset{\text{[For 0–0]}}{(-1) \times 4} + \underset{\text{[For 0]}}{1 \times (-2)}$$

$$x - 6 = 0 \quad x = +6$$

208. In d-d transition, an electron in a d-orbital of the metal is excited by a photon to another d-orbital of higher energy.

Paramagnetism The complex compound which contains unpaired electrons shows paramagnetism while which contains paired electrons shows diamagnetism.

The complex which contains unpaired electrons exhibit d-d transition and paramagnetism.

(i) **In MnO_4^-** The electronic configuration of Mn^{7+} is $[Ar]\ 3d^0$.

Number of unpaired electrons = 0

Therefore, it will be diamagnetic and will not show d-d transition.

(ii) **In $Cr_2O_7^{2-}$** The electronic configuration of Cr^{6+} is $[Ar]3d^0$.

Number of unpaired electrons = 0

So, it will be diamagnetic and will not show *d-d* transition.

(iii) **In CrO_4^{2-}** The electronic configuration of Cr^{6+} is $[Ar]3d^0$.

Number of unpaired electrons = 0

Therefore, it is also diamagnetic and will not show *d-d* transition.

(iv) **In MnO_4^{2-}** The electronic configuration of Mn^{6+} is$[Ar]3d^1$.

Number of unpaired electrons = 1

Since, it contains one unpaired electron so it will exhibit both *d-d* transition and paramagnetism.

209. The reaction of aqueous $KMnO_4$ with H_2O_2 in acidic medium is

$$3H_2SO_4 + 2KMnO_4 + 5H_2O_2 \longrightarrow 5O_2 + 2MnSO_4 + 8H_2O + K_2SO_4$$

In the above reaction, $KMnO_4$ oxidises H_2O_2 to O_2 and itself, i.e. $[MnO_4^-]$ gets reduced to Mn^{2+} ion as $MnSO_4$. Hence, aqueous solution of $KMnO_4$ with H_2O_2 yields Mn^{2+} and O_2 in acidic conditions.

210. Electronic configuration of $_{63}Eu$
$= [Xe]_{54}\ 4f^7 6s^2$

Electronic configuration of $_{64}Gd$
$= [Xe]_{54}\ 4f^7 5d^1 6s^2$

Electronic configuration of $_{65}Tb$
$= [Xe]_{54}\ 4f^9 6s^2$

211. Because of the lanthanoid contraction Zr (atomic radii 160 pm) and Hf (atomic radii 158 pm) have nearly same atomic radii.

Lanthanoids include the elements from lanthanum La ($Z = 57$) to lutetium Lu($Z = 71$). Zirconium Zr (40) Zr (40) belong to the second transition series (4*d*) and Hf (72) belongs to third transition series (5*d*). Lanthanoid contraction is associated with the intervention of the 4*f* orbitals which are filled before the 5*d*-series of elements. The filling of 4*f*-orbitals before 5*d*-orbitals results in regular decrease in atomic radii which compensates the expected increase in atomic size with increasing atomic number. As a result of this lanthanoid contraction, the elements of second and third transition series have almost similar atomic radii.

212. The regular decrease in the radii of lanthanide ions from La^{3+} to Lu^{3+} is known as **lanthanide contraction**.

It is due to the greater effect of the increased nuclear charge than that of screening effect (shielding effect).

As a result of lanthanide contraction, the atomic radii of element of 4*d* and 5*d* come closer, so the properties of 4*d* and 5*d*-transition element shows the similarities.

213. Colour is obtained as a consequence of *d-d* (or *f-f*) transition, and for *d-d* (or *f-f*) transition, presence of unpaired electrons is the necessary condition.

Electronic configuration of

La^{3+} ($Z = 57$) = $[Xe]\ 4f^0 5d^0 6s^0$
(no unpaired electron)

Ti^{3+} (Z = 22) = $[Ar]\ 3d^1 4s^0$
(one unpaired electron)

Lu^{3+} (Z = 71) = $[Xe] 4f^{14} 5d^0 6s^0$
(no unpaired electron)

Sc^{3+} (Z = 21) = $[Ar]\ 3d^0 4s^0$
(no unpaired electron)

Hence, due to the presence of unpaired electron in Ti^{3+}, it exhibit colour in aqueous solution.

214. The reason for greater range of oxidation states in actinoid is attributed to the 5*f*, 6*d* and 7*s* levels having comparable energies.

The 5*f*-orbitals extend into space beyond the 7*s* and 6*p*-orbitals and participate in bonding. This is in direct contrast to the lanthanides where the 4*f*-orbitals are buried deep inside the atom, totally shielded by outer orbitals and thus unable to take part in bonding.

215. More number of oxidation states are exhibited by the actinides than by the corresponding lanthanides due to lesser energy difference between 5*f* and 6*d*-orbitals than that between 4*f* and 5*d*-orbitals.

23. *Coordination Compounds*

216. According to Werner's theory,

$CoCl_3 \cdot 6NH_3 \longrightarrow [Co(NH_3)_6]^{3+} 3Cl^-$

$CoCl_3 \cdot 5NH_3 \longrightarrow [Co(NH_3)_5Cl]^{2+} 2Cl^-$

$CoCl_3 \cdot 4NH_3 \longrightarrow [Co(NH_3)_4Cl_2]^+ Cl^-$

When $AgNO_3$ in excess is treated with these complexes then following reactions takes place :

$$[Co(NH_3)_6]^{3+} 3Cl^- + \underset{\text{(Excess)}}{AgNO_3} \longrightarrow 3AgCl + [Co(NH_3)_6]^{3+}$$

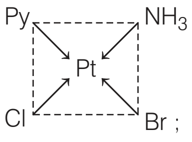
$$[Co(NH_3)_5Cl]^{2+} 2Cl^- + \underset{\text{(Excess)}}{AgNO_3} \longrightarrow 2AgCl + [Co(NH_3)_5Cl]^{2+}$$

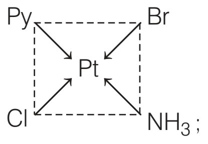
$$[Co(NH_3)_4Cl_2]^+ Cl^- + \underset{\text{(Excess)}}{AgNO_3} \longrightarrow AgCl + [Co(NH_3)_4Cl_2]^+$$

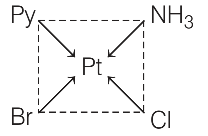
217. The complexes $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are the examples of coordination isomerisms.

This isomerism occurs only in those complexes in which both cation and anion are complex. It occurs due to exchange of ligands between cation and anion.

218. The complex is square planar and is of the type $[M(abcd)]$. It has three geometrical isomers.

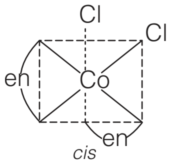




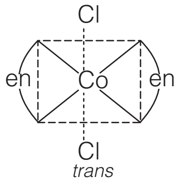


219. $[Co(en)_2Cl_2]Cl$

Possible isomers are



cis
Optically active
stereoisomers =2



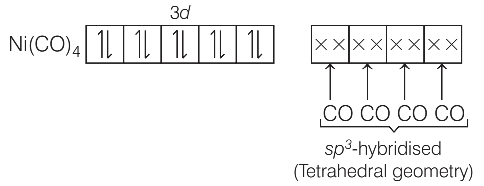
trans
Optically inactive
stereoisomers =1

Hence, total number of stereoisomers = 2 + 1 = 3

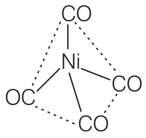
220. The complexes having sp^3-hybridisation are tetrahedral while having dsp^2-hybridisation are square planar. The magnetic behaviour of complexes can be paramagnetic and diamagnetic based on the presence and absence of unpaired electrons, respectively.

Electronic configuration of Ni ($Z = 28$) is $[Ar]_{18}\ 3d^8 4s^2$. Due to presence of CO (neutral ligand), oxidation state of Ni in $[Ni(CO)_4]$ is 0.

Since, CO is a strong field ligand, it pair up the unpaired electrons of Ni.



There is no unpaired electron, hence, $Ni(CO)_4$ is diamagnetic with tetrahedral geometry.



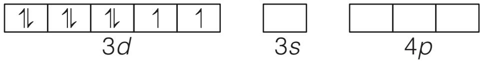
221. $[Ni(CN)_4]^{2-}$

Let oxidation state of Ni in $[Ni(CN)_4]^{2-}$ is x.

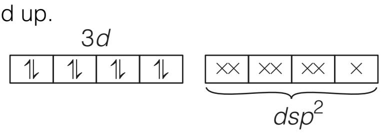
$\therefore \quad x - 4 = -2$

or $\quad x = 2$

Now, $Ni^{2+} = [Ar]\ 3d^8\ 4s^0$



$\because CN^-$ is a strong field ligand. Hence, all unpaired electrons are paired up.



$\therefore$ Hybridisation of $[Ni(CN)_4]^{2-}$ is dsp^2.

222. Optical isomerism is exhibited only by those complexes in which plane of symmetry are absent. Octahedral complexes of the types $[M(aa)_3]$, $[M(aa)x_2, y_2]$ and $[M(aa)_2 x_2]$ have absence of plane of symmetry, thus exhibit optical isomerism. Here, (aa) represents bidentate ligand, x or y represents monodentate ligand and M represents central metal ion.

Hence, $[Co(NH_3)_3Cl_3]^0$ due to presence of symmetry elements does not exhibit optical isomerism.

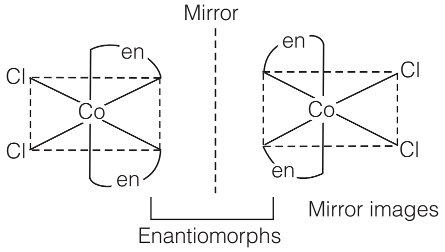
or

Octahedral complexes of $[M(AA)_2B_2]$ type, e.g. $[Co(en)_2Cl_2]^+$, $[M(AA)B_2C_2]$ type, e.g. $[Co(en)Cl_2(NH_3)_2]$ and $[M(AA)_3]$ type, e.g. $[Co(en)_3]^{3+}$ show optical isomerism, whereas complexes of $[MA_3B_3]$ type, e.g. $[Co(NH_3)_3Cl_3]^0$ do not show optical isomerism.

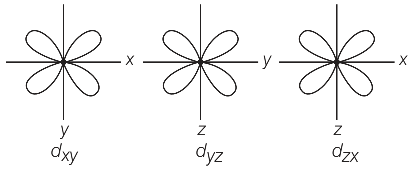
223. Enantiomorphs or Enantiomers A pair of molecules related to each other as an object and its mirror images are known as enantiomorphs or enantiomers. These are not superimposable on its mirror image.

The example is $[Co(en)_2Cl_2]^+$.

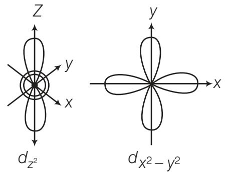
Dichlorobis (ethylenediamine) cobalt (III)



224.

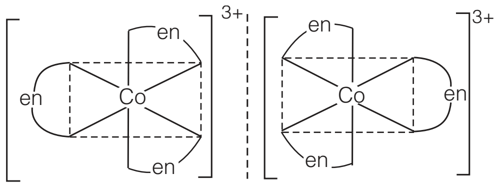


Thus, d_{xy}, d_{yz} and d_{zx} orbitals have maximum electron density between the axis.



d_{z^2} and $d_{x^2-y^2}$ orbitals have maximum electron density along the axis.

225. *tris*-(ethylenediamine) cobalt (III) bromide $[Co(en)_3]Br_3$ exhibits optical isomerism :

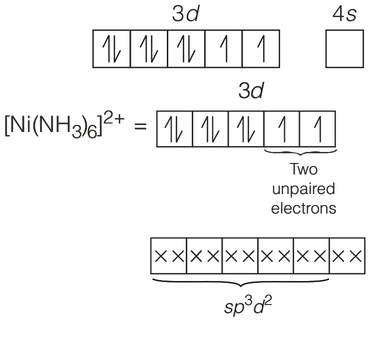


d-form Mirror *l*-form

226. Outer orbital complex utilises $(n-1)d$-orbitals for bonding and exhibit paramagnetic behaviour, only if there present unpaired electrons.

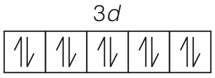
(a) In $[Ni(NH_3)_6]^{2+}$:

$Ni^{2+} = [Ar]\ 3d^8\ 4s^0$

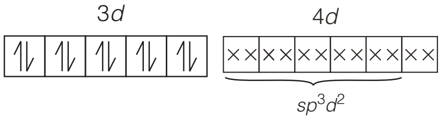


So, this is an outer orbital complex as it involve 4*d*-orbitals for bonding, but having paramagnetic character.

(b) In $[Zn(NH_3)_6]^{2+}$: Zn^{2+} = [Ar] $3d^{10}$



$[Zn(NH_3)_6]^{2+}$ =

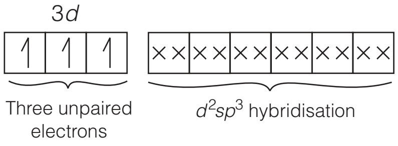


Thus, it is also an outer orbital complex as it involve 4*d*-orbitals for bonding but it is diamagnetic as all the electrons are paired.

(c) In $[Cr(NH_3)_6]^{3+}$:

Cr^{3+} = [Ar] $3d^3$

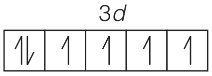
$[Cr(NH_3)_6]^{3+}$ =



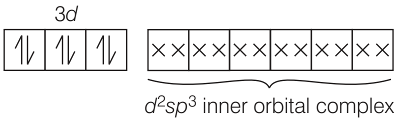
Because of the involvement of $(n-1)d$, i.e. 3*d*-orbital in hybridisation, it is an inner orbital complex. Its nature is paramagnetic because of the presence of three unpaired electrons.

(d) In $[Co(NH_3)_6]^{3+}$:

Co^{3+} = [Ar] $3d^6$



$[Cr(NH_3)_6]^{3+}$ =



Because of the involvement of $(n-1)d$ orbital in hybridisation, it is an inner orbital complex. As all the electrons are paired, it is a diamagnetic complex.

227. The electronic configuration of

$V(23)$ = [Ar] $4s^2, 3d^3$

Let in $[V(gly)_2(OH)_2(NH_3)_2]^+$ oxidation state of V is *x*.

$$x + (-1) \times 2 + (-1)2 + (0 \times 2) = +1$$
$$x = +5$$

V^{5+} = [Ar] $4s^0, 3d^0$ (no unpaired electrons)

The electronic configuration of Fe(26) = [Ar] $4s^2, 3d^6$

Let the oxidation state of Fe in $[Fe(en)(ppy)(NH_3)_2]^{2+}$ is *x*.

$$[x + (0) + (0) + (0) \times 2] = +2$$
$$x = +2$$

Fe^{2+} = [Ar], $3d^6$ ($\because$ 4 unpaired electron)

but, bpy, en and NH_3 all are strong field ligands, so pairing occurs and thus, Fe^{2+} contains no unpaired electron.

The electronic configuration of

Co(27) = [Ar] $4s^2, 3d^7$

Let the oxidation state of Co in $[Co(ox)_2(OH)_2]^-$ is *x*.

$$x + (-2) \times 2 + (-1) \times 2 = -1$$
$$x = +5$$

Co^{5+} = [Ar], $3d^4$ [4 unpaired electrons]

ox and OH are weak field ligands, thus pairing of electron units does not occur.

The electronic configuration of Ti(22) = [Ar] $4s^2, 3d^2$

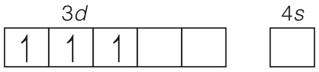
Oxidation state of Ti in $[Ti(NH_3)_6]^{3+}$ is 3.

Ti^{3+} = [Ar] $3d^1$ (one unpaired electron)

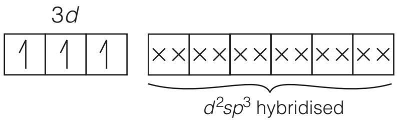
Hence, complex $[Co(ox)_2(OH)_2]^-$ has maximum number of unpaired electrons, thus show maximum paramagnetism.

228. In $[Cr(NH_3)_6]^{3+}$, Cr is present as Cr^{3+}.

Cr^{3+} = [Ar] $3d^3, 4s^0$



$[Cr(NH_3)_6]^{3+}$ = [Ar] $3d^3$



Since, this complex has three unpaired electrons, excitation of electrons is possible and thus, it is expected that this complex will absorb visible light.

229. Magnetic moment $(\mu) = \sqrt{n(n+2)}$ BM

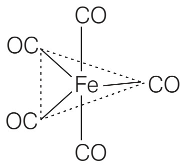
or $3.83 = \sqrt{n(n+2)}$

or $3.83 \times 3.83 = n^2 + 2n$

$14.6689 = n^2 + 2n$

$n \simeq 3$

Hence, number of unpaired electrons in *d*-subshell of chromium (Cr = 24) = 3.



So, the configuration of chromium ion is

$$Cr^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3$$

In $[Cr(H_2O)_6]Cl_2$, oxidation state of Cr is +3.

Hence, in $3d^3$ the distribution of electrons

$$3d^1_{xy}, 3d^1_{yz}, 3d^1_{zx}, 3d^0_{x^2-y^2}, 3d^0_{z^2}$$

230. The CFSE for octahedral complex is given by

$$\text{CFSE} = [-0.4\, t_{2g}e^- + 0.6\, e_g e^-]$$

For $Mn^{3+}, [3d^4] \rightarrow t^3_{2g}e^1_g$

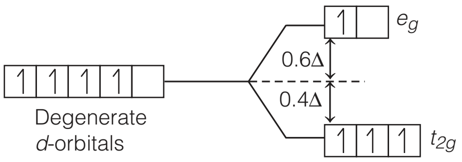
$\therefore$ CFSE = $[(-0.4 \times 3) + (0.6 \times 1)] = -0.6$

For $Fe^{3+}, [3d^5] \rightarrow t^3_{2g}e^2_g$

CFSE = $[-(0.4 \times 3) + (0.6 \times 2)] = 0$

231. In case of high spin complex, Δ_o is small. than the pairing energy. That means, the energy required to pair up the fourth electron with the electrons of lower energy *d*-orbitals would be higher than that required to place the electrons in the higher *d*-orbital. Thus, pairing does not occur.

For high spin d^4 octahedral complex,



∴ Crystal field stabilisation energy

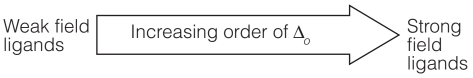
$$= (-3 \times 0.4 + 1 \times 0.6)\,\Delta_o$$
$$= (-1.2 + 0.6)\,\Delta_o = -0.6\,\Delta_o$$

232. Wavelength (λ) of absorption is inversely proportional to CFSE (Δ_o value) of ligands attached with the central metal ion.

i.e. $$\lambda \propto \frac{1}{\Delta_o}$$

According to spectrochemical series.

$$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-}$$
$$< H_2O < NSS^- < NH_3 < en < NO_2^- < CN^-$$



The CFSE of ligands attached with Co^{3+} ion is in the order en > NH_3 > H_2O (From spectrochemical series)

∵ Wavelength of absorbed light $(\lambda) \propto \frac{1}{\Delta_o}$.

∴ For ligand the order of wavelength of absorption in the visible region will be : en < NH_3 < H_2O

or, $[Co(en)_3]^{3+} < [Co(NH_3)_6]^{3+} < [Co(H_2O)_6]^{3+}$

233. Compounds of transition metal with carbonyls (carbon monoxide) are known as metal carbonyls. These are classified into mononuclear, dinuclear, trinuclear and so on based on the number of central metal atoms/ions present in a complex.

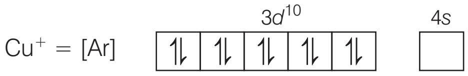
Complexes following EAN rule have EAN of central metal/ion equal to nearest inert gas configuration and hence, are stable.

Effective atomic number (EAN) of the metal in a complex is given by

EAN = Atomic number (*Z*) – Oxidation number (O.N) + 2 (Coordination number)

= 26 – 0 + 2 (5) = 36

Thus, $Fe(CO)_5$ is a stable complex/ion. Since, there is only one central metal atom present in iron carbonyl, $Fe(CO)_5$, thus it is mononuclear. The structure of $Fe(CO)_5$ is shown below:



The examples of dinuclear, trinuclear complexes are $Co_2(CO)_{18}$ and $Fe_3(CO)_{12}$ respectively.

234. As negative charge on metal carbonyl complex increases, back π-bonding increases and hence bond length of C—O bond increases while bond length of metal-carbon bond decreases.

Hence, $[Fe(CO)_4]^{2-}$ has longest C—O bond length among the given complexes.

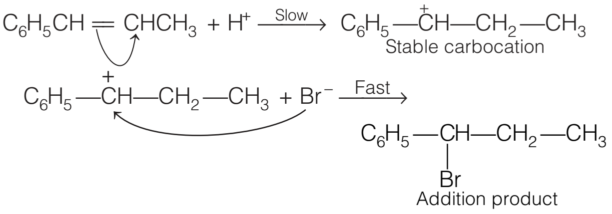
The correct order of bond length of the given complexes is

$[Mn(CO)_6]^+ < [Ni(CO)_4] < [Co(CO)_4]^- < [Fe(CO)_4]^{2-}$

24. *Haloalkanes and Haloarenes*

235. In (I) and (IV) due to the presence of Lucas reagent (HCl + anhy. $ZnCl_2$) alcohols give alkyl halides while in (III) alkyl halide is formed due to S_N1 reaction.

236.



Electrophilic addition reaction takes place *via* more stable carbocation.

237. $$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{Anti - Markownikoff' s rule}]{HBr / H_2O_2} CH_3CH_2CH_2CH_2Br$$

Bromo butane (1° product)

$$CH_3CH_2CH_2CH_2Br \xrightarrow[S_N2 \text{ reaction}]{C_2H_5\overset{-}{O}\overset{+}{Na}} CH_3CH_2CH_2CH_2OC_2H_5$$

(Williamson's synthesis)

Ethoxy-butane

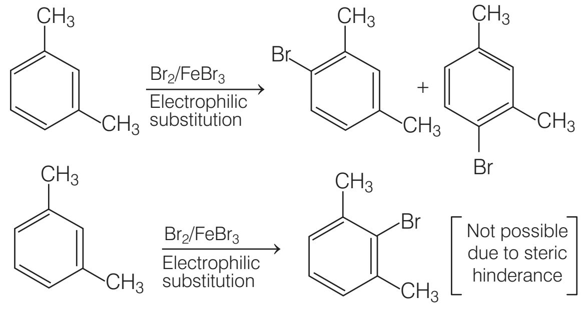
238. A protic solvents like DMF increases the reactivity of nucleophile and favours S_N2 reaction.

The relative reactivity of alkyl halides towards S_N2 reactions is as follows :

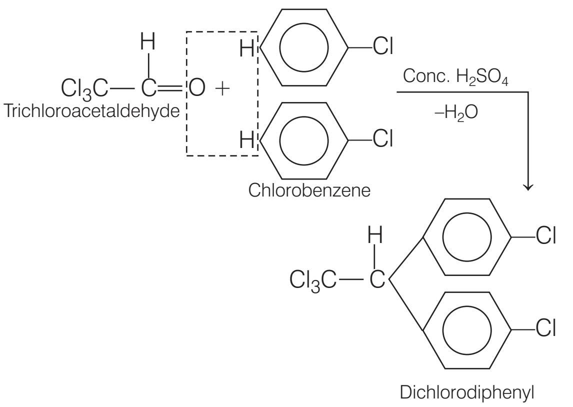
CH_3 —*X* > Primary > Secondary > Tertiary

However, if the primary alkyl halide or the nucleophile/base is sterically hindered the nucleophile will have difficulty to getting the back side of the α-carbon as a result of this, the elimination product will be predominant. Here, CH_3CH_2Br is the least hindered, hence it has the highest relative rate towards S_N2 reaction.

239. CH_3 is a *o*/*p*-directing group, thus electrophilic substitution reaction of toluene.



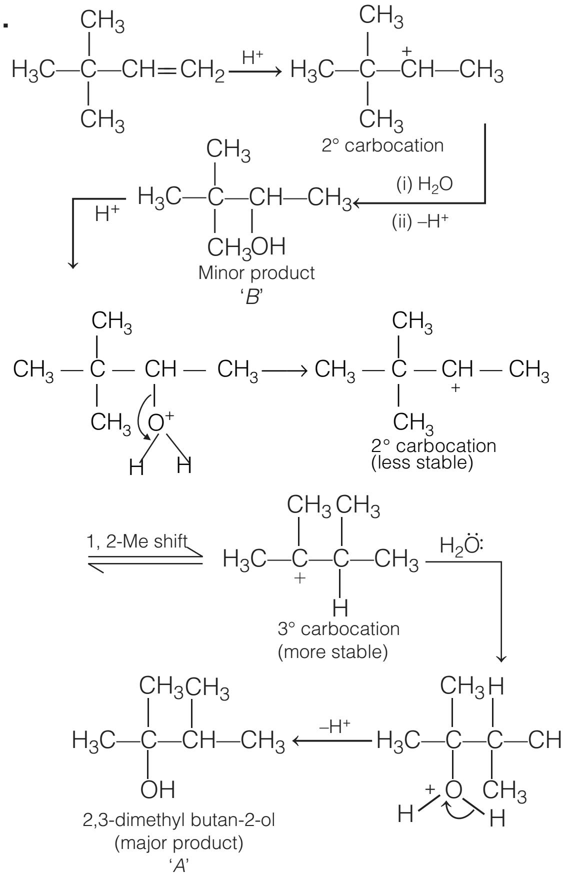
240.



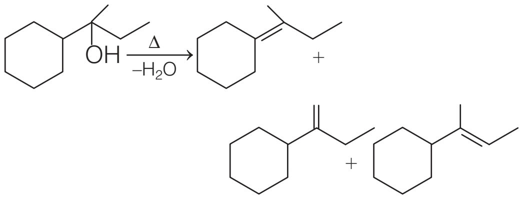
Dichlorodiphenyl trichloroethane (DDT)

25. *Alcohols, Phenols and Ethers*

241.



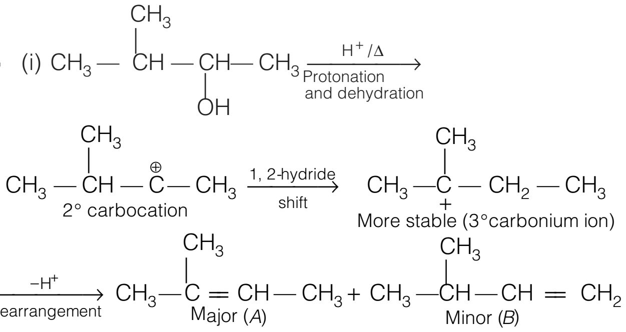
242. When intermediate carbocation is stable, no rearrangement takes place in carbocation.



243. $$\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{PBr_3} C_2H_5Br \xrightarrow[\substack{-KBr\\ -H_2O\\ \beta\text{-elimination}}]{\text{Alc. KOH}} CH_2=CH_2$$

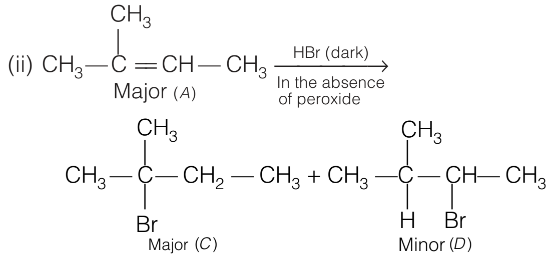
$$\xrightarrow{H_2SO_4} CH_3-CH_2OSO_3H \xrightarrow[-H_2SO_4]{H_2O/\Delta} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

244. (i)

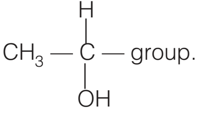


A part is major because more substituted alkenes are more stable.

(ii)



245. An organic compound form yellow precipitate of iodoform with I_2 in presence of alkali, if it has CH_3CO —group directly or it has

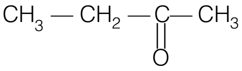


$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-$ group.

(a) $CH_3CH(OH)CH_3 + I_2 \xrightarrow{NaOH} CH_3COCH_3 + 2HI + 3NaI + CH_3COO^-Na^+ + 3H_2O$

$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + 3NaI + CH_3COO^-Na^+ + 3H_2O$

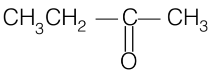
(b) $CH_2-CH_2CH(OH)\,CH_3 + I_2 \longrightarrow$



$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + 2HI$

Ethyl methyl ketone

It gives iodoform test.



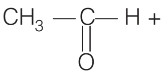
$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + 3I_2 + 4NaOH \longrightarrow$

$\underset{\text{Yellow ppt.}}{CHI_3\downarrow} + 3NaI + CH_3CH_2COONa + 3H_2O$

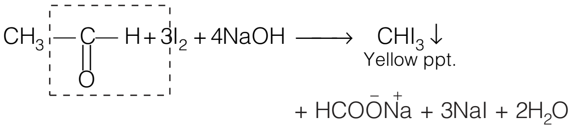
(c) $CH_3OH + I_2 \longrightarrow HCHO + 2HI$

It does not have methyl ketonic group, so it does not give yellow ppt. with I_2 in presence of alkali.

(d) $CH_3CH_2OH + I_2 \longrightarrow$



$CH_3-\underset{\underset{O}{\|}}{C}-H + 2HI$



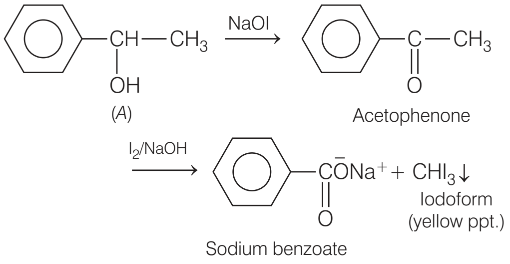
$$CH_3-\underset{\underset{O}{\|}}{C}-H+3I_2+4NaOH \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3\downarrow} + HCO\overset{-}{O}\overset{+}{Na} + 3NaI + 2H_2O$$

Due to the presence of —$COCH_3$ group, it gives Haloform test.

246. Iodoform reaction with sodium hypoiodite is used for the detection of CH_3CO group. Also compounds containing $CH_3CH(OH)$ group shows positive iodoform test as it produces CH_3CO group on oxidation.

Since, among the compounds, $CH_3CH(OH)$ group is given only in the substrate of option (a) hence, it is correct. The reaction of compound *A* with NaOI is given as follows :

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$



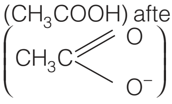
247. This problem is based on the acidic character of phenol. Electron -withdrawing group at *o* and *p*-position w.r.t. —OH group of phenol, increase the acidic strength.

Picric acid (2, 4, 6-trinitrophenol) is extremely more acidic than given compounds because its pK_a value is close to zero also due to the presence of three strong electron withdrawing group (—NO_2 group) at *ortho* and *para*-positions, picric is more acidic compound.

248. Higher the tendency to give a proton, higher is the acidic character and tendency to lose a proton depends upon the stability of intermediate, i.e. carbanion formed.

2, 4, 6-trinitrophenol after the loss of a proton gives 2,4,6-trinitrophenoxide ion which is stabilised by resonance, –*I*-effect and –*M*-effect, thus is most acidic among the given compounds.

Phenol after losing a proton form phenoxide ion which is also stabilised by resonance, – *M* and – *I* effects but is less stabilised as compared to 2, 4, 6-trinitrophenoxide ions. Thus, it is less acidic as compared to 2, 4, 6-trinitrophenol. (CH_3COOH) after losing a proton gives acetate



$$\left(CH_3C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown O^-\end{matrix}\right)$$ ion which is stabilised by only resonance.

Carboxylate ion

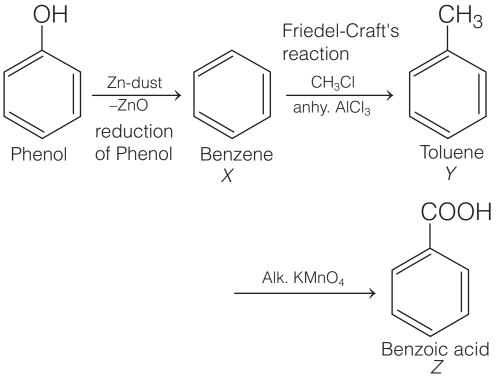
However, it is more resonance stabilised as compared to a phenoxide ion, thus more acidic as compared to phenol. 2, 4, 6-trinitrophenol, however, is more acidic than acetic acid due to the presence of three electron withdrawing —NO_2 groups. Cyclohexanol gives an anion that is least stable among the given, thus, it is least acidic.

Hence, the correct order of acidic strength is

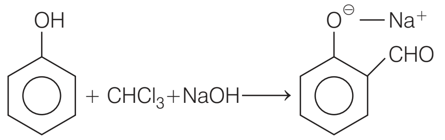
2, 4, 6-trinitrophenol > acetic acid > phenol > cyclohexanol

III > II > IV > I

249.



250.



The above given reaction is known as Riemer-Tiemann reaction. In this reaction, electrophile involved is dichlorocarbene ($:CCl_2$) which is formed in the Ist step of mechanism. It is given as follows :

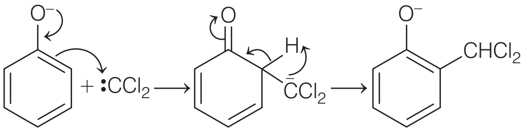
Mechanism

***Step* I** Generation of electrophile

$$CHCl_3 + OH^- \rightleftharpoons {}^-CCl_3 + H_2O$$

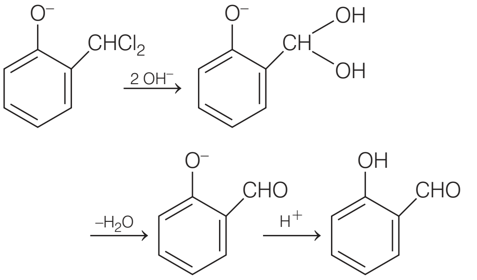
$${}^-CCl_3 \longrightarrow \underset{\substack{\text{(Electrophile)}\\ \text{Dichlorocarbene}}}{:CCl_2} + Cl^-$$

***Step* II** Reaction of etectrophile with phenoxide



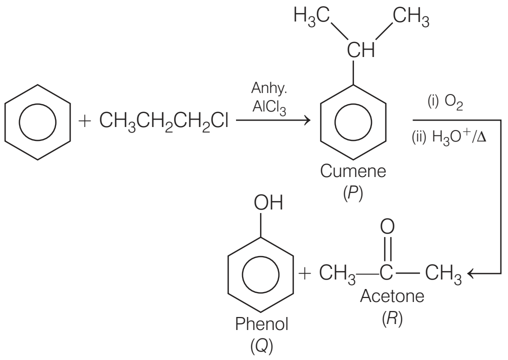
o-dichloromethyl phenoxide

***Step* III** Hydrolysis



Salicylaldehyde

251. The given reaction takes place as follows :



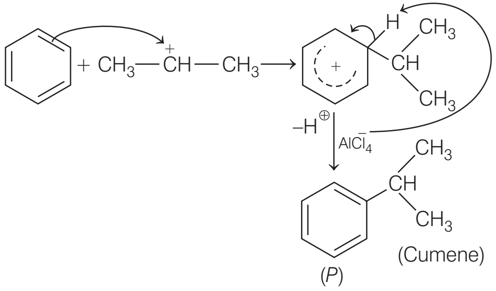
Mechanism

***Step* I** Formation of carbocation.

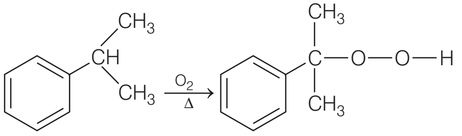
$$CH_3CH_2CH_2—Cl + AlCl_3 \longrightarrow CH_3CH_2\overset{+}{C}H_2 + Al\overset{-}{Cl}_4$$

$$\underset{\substack{\text{Carbocation}\\(1°)}}{CH_3CH_2\overset{+}{C}H_2} \xrightarrow{1,\,2\,H^-\text{ shift}} \underset{\substack{\text{Carbocation}\\(2°)}}{CH_3\overset{+}{C}H—CH_3}$$

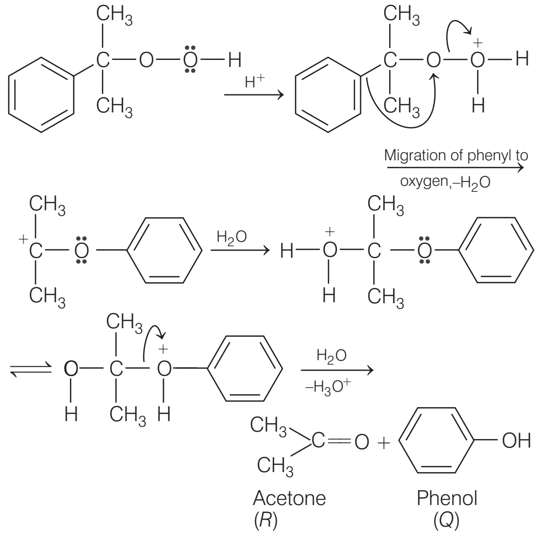
***Step* II** Electrophilic substitution reaction.



***Step* III** Formation of peroxide.



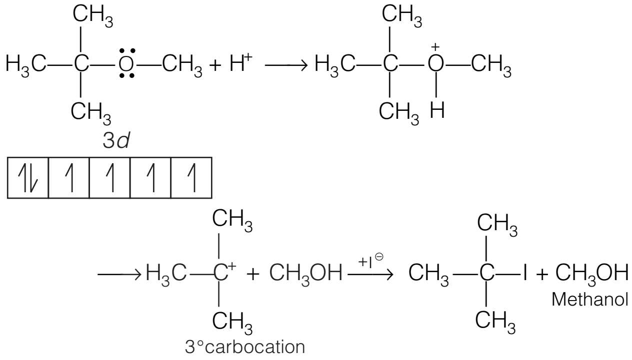
***Step* IV** Hydrolysis of oxidised product formed in step III.



252. The ether which gives more stable carbocation, forms CH_3OH as one of the product with hot conc. HI. The order of stability of carbocation is 3° > 2° > 1°.

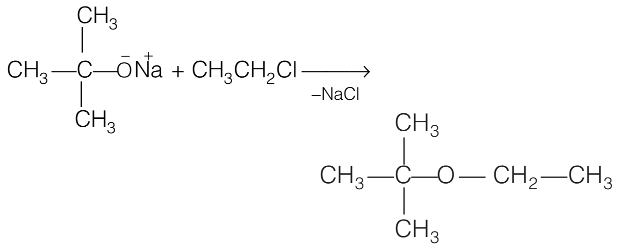
Thus, $CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OCH_3$ gives CH_3OH as one of the product.

The reaction proceeds as :



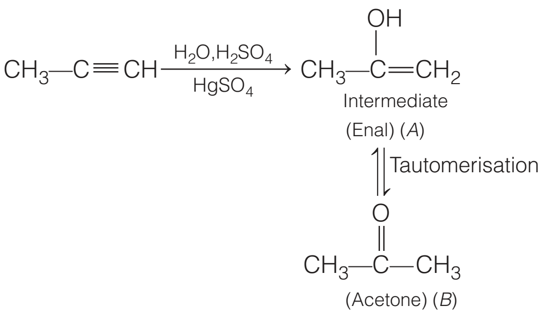
253. The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called **Williamson synthesis**. Here, in this reaction alkyl halide should be primary and alkoxide, should be bulkier as shown below :

$$\underset{\substack{\text{Alkyl}\\\text{halide}}}{R—X} + \underset{\text{Sodium alkoxide}}{R'—\overset{-}{O}\overset{+}{Na}} \longrightarrow \underset{\text{Ether}}{R—O—R'} + NaX$$



26. *Aldehyde, Ketone and Carboxylic Acid*

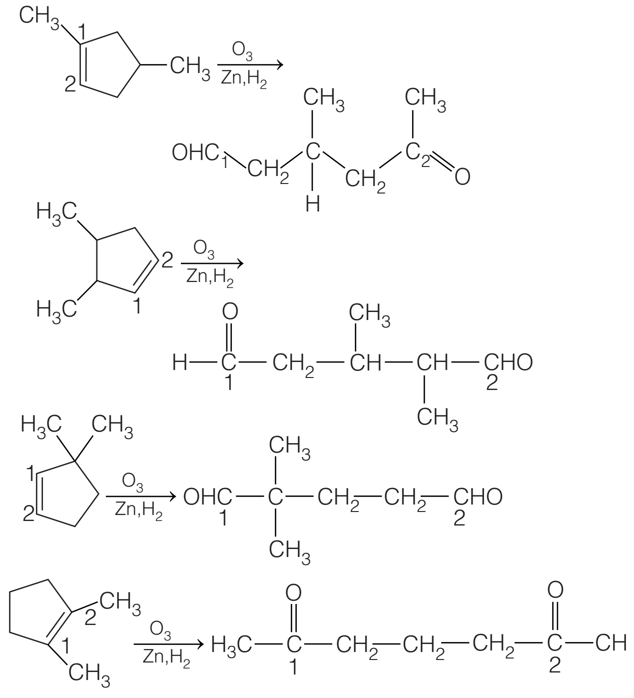
254.



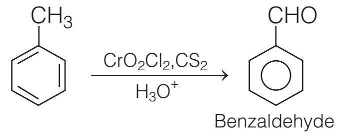
Therefore, $A = CH_3—\overset{OH}{C}=CH_2$

$B = CH_3—\overset{O}{\overset{\|}{C}}—CH_3$

255.

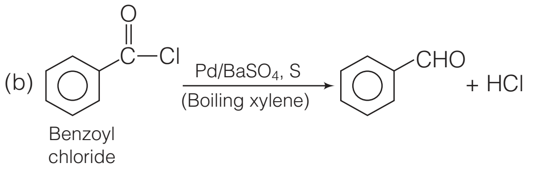


256.



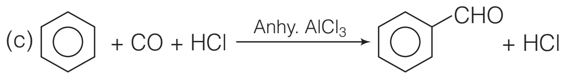
This reaction is known as **Etard reaction**.

(b)



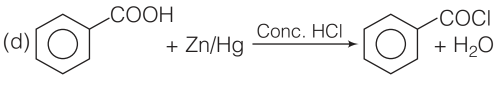
This reaction is called **Rosenmund reaction**.

(c)



The above reaction is known as **Gattermann-Koch** aldehyde synthesis.

(d)

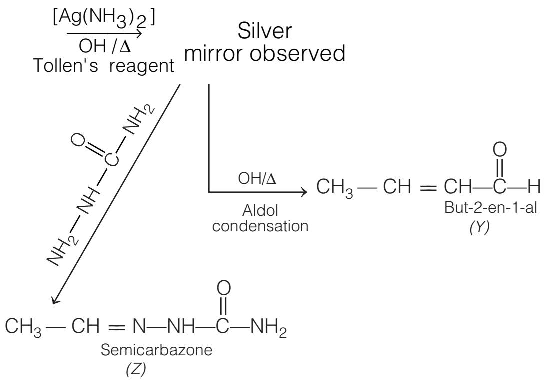


Thus, from the reactants given in option (d) benzaldehyde is not obtained.

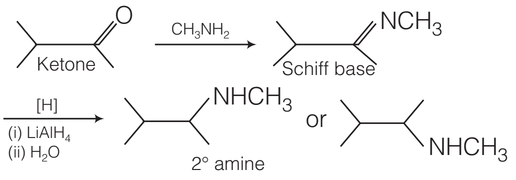
257. Aldehydes gives silver mirror test so, '*X*' may be alcohol which is oxidised by Cu gives aldehydes.

Therefore, *X* is acetaldehyde (CH_3CHO).

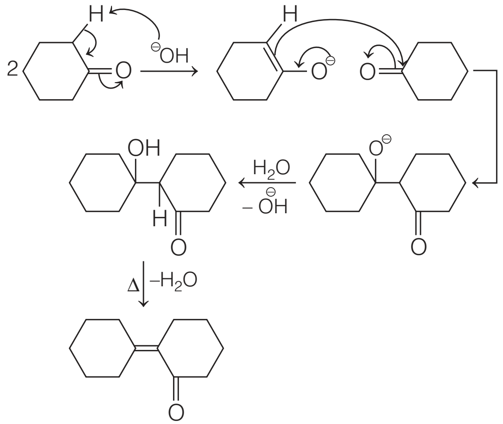
$$\underset{(A)}{C_2H_5OH} \xrightarrow[\text{oxidation}]{\text{Cu/573 K}} \underset{\substack{\text{Acetaldehyde}\\(X)}}{CH_3CHO}$$



258.



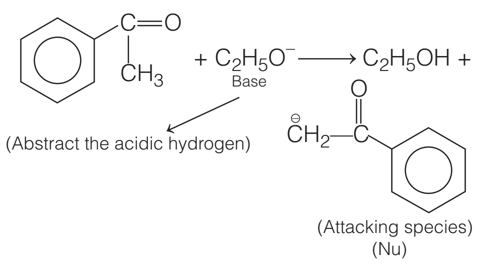
259. Aldehydes and ketones containing α-H atoms undergo aldol condensation in presence of dilute alkali as catalyst and gives α, β-unsaturated compound with the elimination of H_2O molecule.

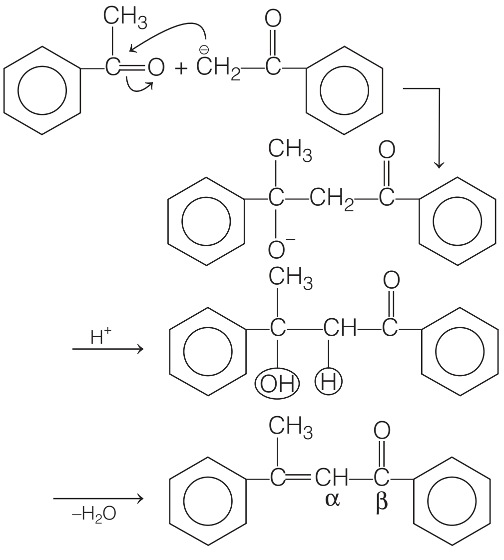


(α, β- unsaturated compound)

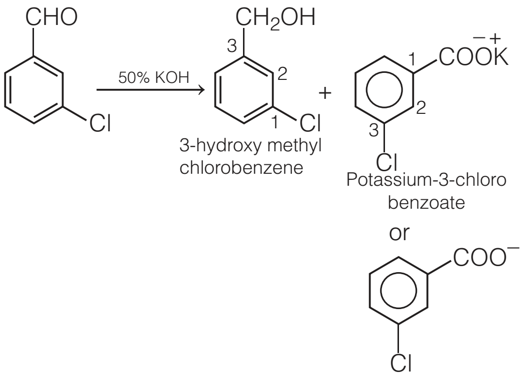
260. Aldehydes and ketones with α-hydrogen atom, when reacted with a base yields aldol which on heating loses water molecule to give α, β-unsaturated aldehydes or ketones. This reaction is called aldol condensation reaction.

$$\underset{\text{Base}}{C_2H_5ONa} \rightleftharpoons C_2H_5O^- + Na^+$$

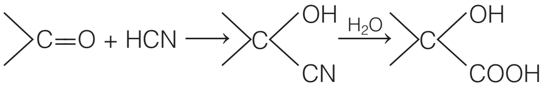




261. When benzaldehyde is treated with 50% alkali, it undergoes oxidation to give an acid salt as well as reduction to give an alcohol. This reaction is called Cannizaro's reaction.



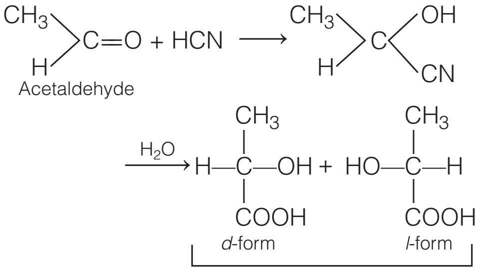
262.



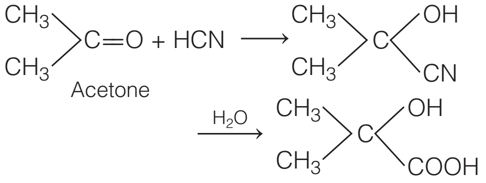
(It is α-hydroxy acid)

In this reaction, complete hydrolysis of cyanide gives acid and partial hydrolysis gives amide.

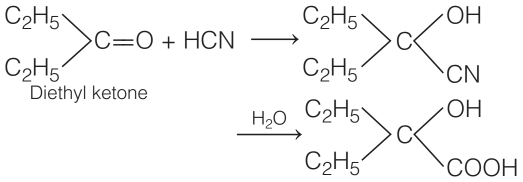
Racemic mixture, is obtained when C-atom is asymmetric.



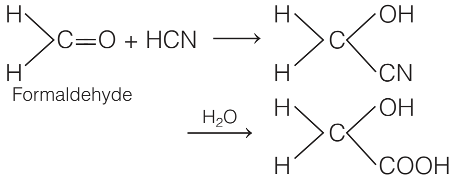
Racemic mixture



It is not optically active, racemic mixture is not formed.



It is not optically active.



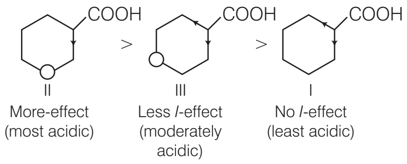
It is not optically active.

263. Order of strengths of the given carboxylic acids can be determined by the concept of *I*-effect.

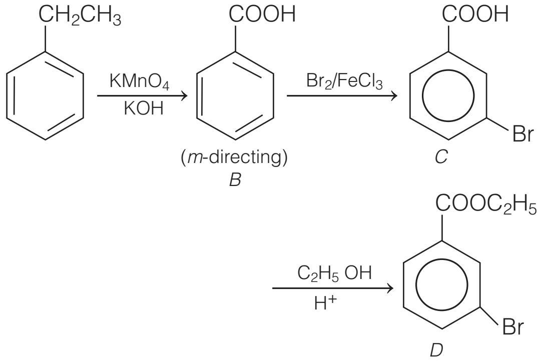
The oxygen atom present in the ring shows *I*-effect. As the distance between oxygen and —COOH group increases, –*I*-effect of oxygen decreases.

Thus, corresponding carboxylic acid will show less acidic nature.

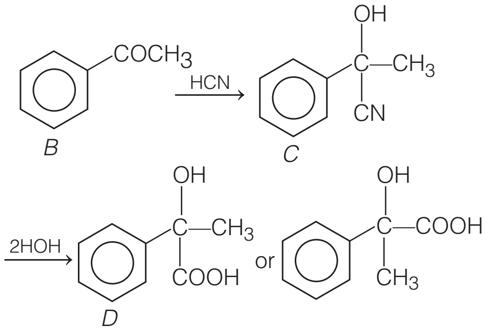
The correct order of strengths of the carboxylic acids is



264. Alkaline $KMnO_4$ converts complete carbon chain (that is directly attached to benzene nucleus) to —COOH group. Br_2 in the presence of halogen carrier causes bromination by electrophilic substitution reaction and ethyl alcohol in acidic medium results in esterification.

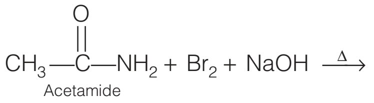


265. $CH_3COOH \xrightarrow{SOCl_2} \underset{A}{CH_3COCl} \xrightarrow[\text{Anhy. }AlCl_3]{\text{Benzene}}$

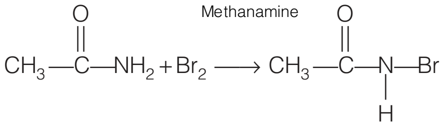


27. *Organic Compound Containing Nitrogen*

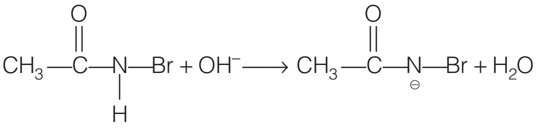
266. The conversion of amide with no substituent on nitrogen to an amine containing one carbon less by the action of alkaline bromamide or bromine in presence of NaOH is known as Hofmann Bromamide reaction. It involves the migration of alkyl or aryl group with its electron pair to electron deficient N from adjacent carbon. The reaction involves the intermediates of isocyanate.



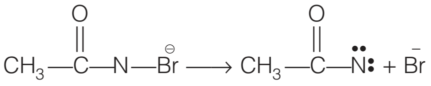
$$\underset{\text{Acetamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + Br_2 + NaOH \xrightarrow{\Delta} \underset{\text{Methanamine}}{CH_3NH_2} + NaBr + Na_2CO_3 + H_2O$$

Step I 

$$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-Br$$

Step II 

$$CH_3-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-Br + OH^- \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\underset{\ominus}{N}-Br + H_2O$$

Step III 

$$CH_3-\overset{O}{\overset{\|}{C}}-N-\overset{\ominus}{Br} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}: + \bar{Br}$$

Step IV 

$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}: \xrightarrow[\text{alkyl migration}]{\text{Intermolecular}} CH_3NCO$$

Step V $CH_3NCO + 2OH^- \xrightarrow{\Delta} CH_3NH_2 + CO_3^{2-}$

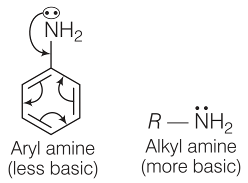
267. Due to resonance in chlorobenzene C—Cl bond acquires double bond character hence, C—Cl bond is inert towards nucleophile (phthalimide ion). Therefore, aniline cannot be prepared.

268. The reagent which can convert —$CONH_2$ group into —NH_2 group is NaOH/Br_2.

Among the given reagents only NaOH/Br_2 converts —$CONH_2$ group to —NH_2 group, thus it is used for converting acetamide to methyl amine. This reaction is called **Hofmann Bromamide reaction**, in which primary amides on treatment with Br_2 / NaOH form primary amines.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + NaOH + Br_2 \longrightarrow \underset{\text{Methyl amine}}{CH_3NH_2} + NaBr + Na_2CO_3 + H_2O$$

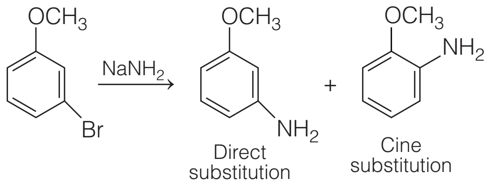
269.



Due to delocalisation of lone pair of electrons of N-atom to the benzene ring, it losses its basicity and becomes less basic than alkyl amine.

On the other hand, alkyl amine has free lone pair of electron as well as + *I*-effect of alkyl group increases electron density on N-atom enhancing its basic nature.

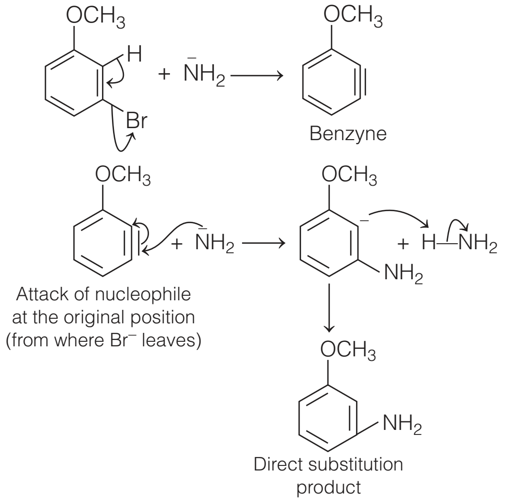
270.

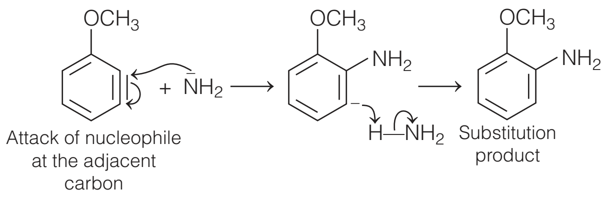


If nucleophile occupies same position of the leaving group, product is called **direct substitution product**.

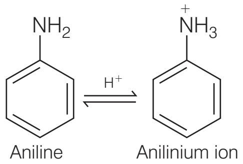
If nucleophile occupies adjacent position of the leaving group, product is called **cine substitution product**.

Intermediate formed in this reaction is benzyne.

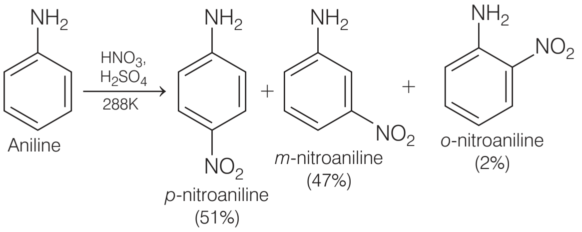




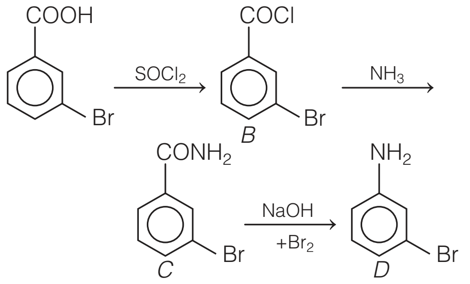
271. In strongly acidic medium, aniline is protonated to form the anilinium ion.



Since, anilinium ion so formed is *meta* directing, thus besides *ortho* and *para*- derivatives, significant amount of *meta* derivative is also formed.

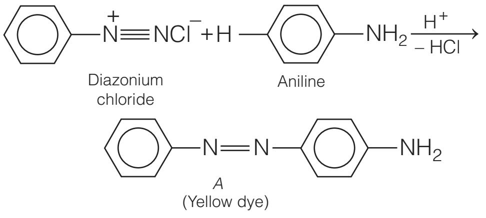


272.



The conversion of '*C*' to '*D*' is an example of Hofmann Bromamide degradation reaction.

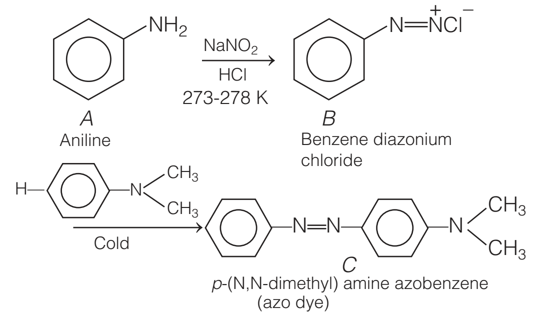
273. The complete reaction is



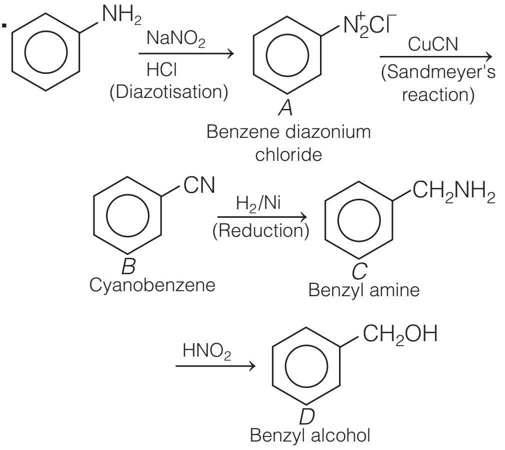
(*p*-azo benzene compound)

The above reaction is a **coupling reaction** of aniline with diazonium salt to give azo benzene compound. This coupling reaction takes place at the *para*-position to —NH_2 group of benzene. This reaction act as electrophilic substitution reaction of aniline.

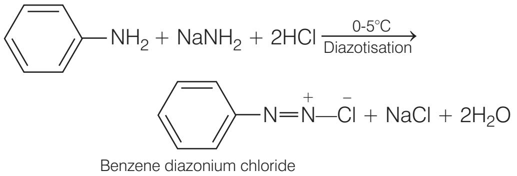
274.



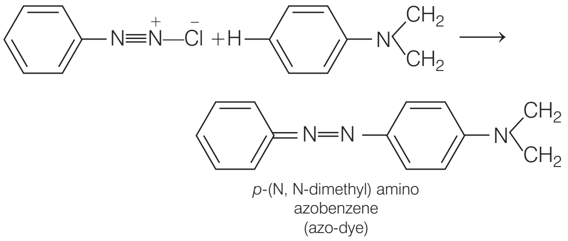
275.



276. Aniline on diazotisation in cold (at 0° to 5° C) gives benzene diazonium chloride.

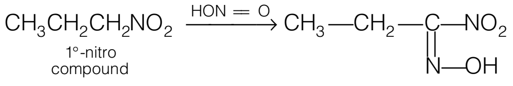


This benzene diazonium chloride on coupling with dimethyl aniline gives a coloured product, i.e. *p*-(N,N-dimethyl) amino azobenzene (azo dye).

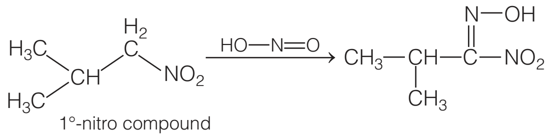


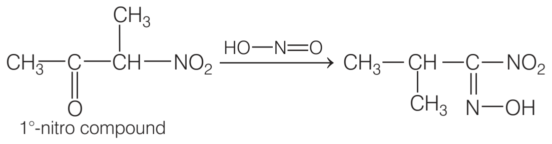
277. 1° and 2° nitro compounds react with HNO_2 while 3°-nitro compound does not.

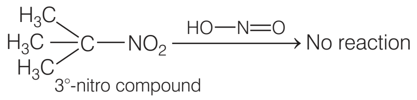
The reactions of given compounds with HNO_2 are as follow:



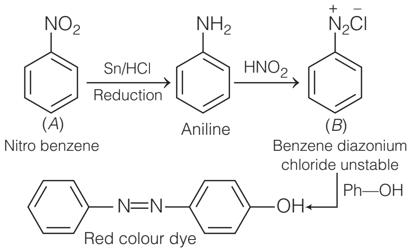
$$\underset{\text{1°-nitro compound}}{CH_3CH_2CH_2NO_2} \xrightarrow{HON=O} CH_3-CH_2-\underset{\underset{N-OH}{\|}}{C}-NO_2$$





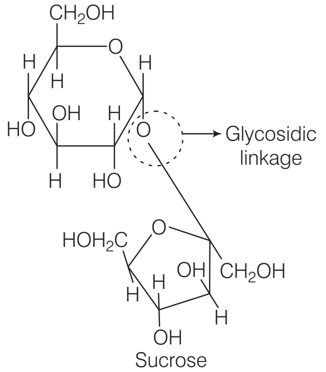


278. The complete road map of the reaction can be seen as:



28. *Biomolecules*

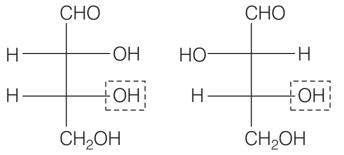
279. Sucrose is non-reducing sugar because reducing part of glucose $(-\overset{\overset{O}{\|}}{C}-H)$ and fructose $(>C=O)$ are involved in glycosidic linkage.



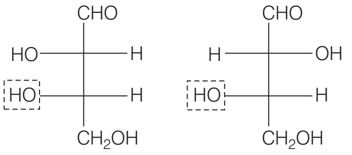
Sucrose

While, lactose, glucose and maltose are reducing sugars.

280.



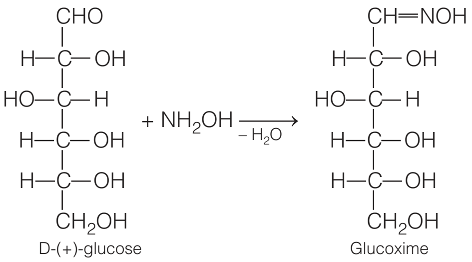
D-erythrose D-threose



L-erythrose L-threose

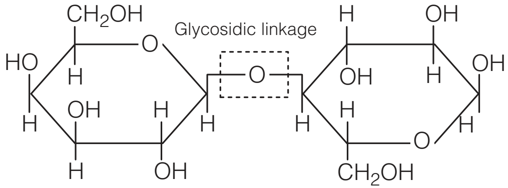
Thus, the correct option is (d).

281. D-(+)-glucose contains aldehydic group which reacts with hydroxyl amine (NH_2OH) to yield an oxime. The complete reaction is



D-(+)-glucose Glucoxime

282.



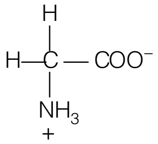
(+)-Lactose

Lactose is a reducing sugar and all reducing sugars show mutarotation.

283. Ion containing positive as well as negative charge is called *Zwitter* ion.

Among the given options, only glycine ($H_2N—CH_2—COOH$) is an amino acid which contains both acidic (acquiring negative charge) and basic group (acquiring positive charge).

Glycine can form a *Zwitter* ion. It is because glycine behave like salts rather than simple amines or carboxylic acids. In aqueous 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.



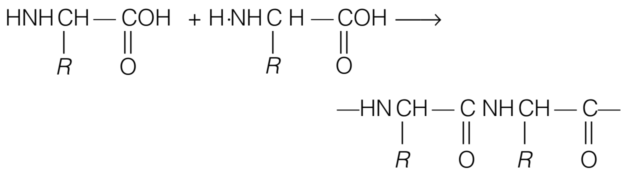
Zwitter ion

Zwitter ion is a cation in acidic medium and migrates to cathode on passing electric current. It is an anion in basic medium and migrates to anode on passing electric current.

284. In the process of digestion the proteins present in food material are hydrolysed to amino acid. In this process two enzymes pepsin and trypsin are involved as follows:

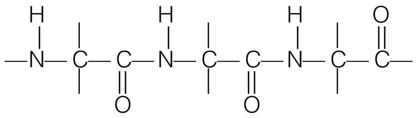
$$\text{Proteins} \xrightarrow[\text{(Enzyme } A)]{\text{Pepsin}} \text{Polypeptide} \xrightarrow[\text{(Enzyme } B)]{\text{Trypsin}} \text{Amino acids}$$

285. The peptide linkage (—NH— CO—) is formed by the condensation of amino acids molecules



$$\mathrm{HNH\underset{\underset{R}{|}}{C}H—\underset{\underset{O}{\|}}{C}OH + H{\cdot}NH\underset{\underset{R}{|}}{C}H—\underset{\underset{O}{\|}}{C}OH} \longrightarrow \mathrm{—HN\underset{\underset{R}{|}}{C}H—\underset{\underset{O}{\|}}{C}NH\underset{\underset{R}{|}}{C}H—\underset{\underset{O}{\|}}{C}—}$$

Hence, following structure represents the peptide chain



$$\mathrm{—\overset{\overset{H}{|}}{N}—\underset{|}{\overset{|}{C}}—\underset{\underset{O}{\|}}{C}—\overset{\overset{H}{|}}{N}—\underset{|}{\overset{|}{C}}—\underset{\underset{O}{\|}}{C}—\overset{\overset{H}{|}}{N}—\underset{|}{\overset{|}{C}}—\overset{\overset{O}{\|}}{C}—}$$

286. Deprotonation of protein occur when it is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. As a result, globules unfolds and helix get uncoiled and protein losses its biological activity.

Hence, the denaturation of protein makes the protein inactive.

287. In DNA, two helically twisted strands connected together by steps. Each strand consists of alternating molecules of deoxyribose at 2′-position and phosphate groups.

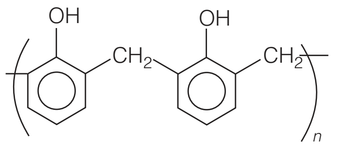
On the other hand, in RNA, the pentose sugar has an identical structure with deoxyribose sugar except that there is an —OH group instead of —H on carbon atom 2′.

Hence, it is only called ribose.

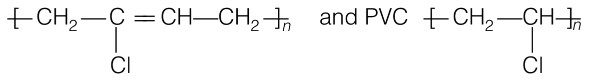
29. *Polymers*

288. Cross-linked or network polymers are formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. These are hard, rigid and brittle due to cross-links, e.g. bakelite, melamine etc. Thus, option (d) is incorrect.

289.

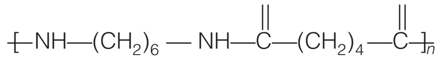


Novolac, a condensation polymer of phenol and formaldehyde is a thermosetting polymer. Neoprene rubber



$$\mathrm{\left[\!—CH_2—\underset{\underset{Cl}{|}}{C}=CH—CH_2—\!\right]_n} \text{ and PVC } \mathrm{\left[\!—CH_2—\underset{\underset{Cl}{|}}{C}H—\!\right]_n}$$

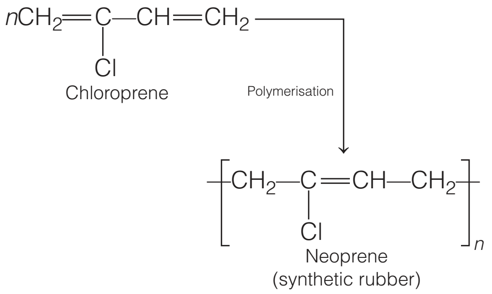
are thermoplastic polymers while nylon-6,6



$$\mathrm{\left[\!—NH—(CH_2)_6—NH—\overset{\overset{O}{\|}}{C}—(CH_2)_4—\overset{\overset{O}{\|}}{C}—\!\right]_n}$$

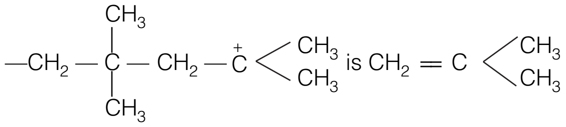
is a polyamide which is commonly known as fibre.

290. Neoprene is a polymer of chloroprene (2-chloro -1,3-butadiene) and also called homopolymer (addition polymer).



$$n\mathrm{CH_2{=}\underset{\underset{Cl}{|}}{C}—CH{=}CH_2} \xrightarrow{\text{Polymerisation}} \mathrm{\left[—CH_2—\underset{\underset{Cl}{|}}{C}{=}CH—CH_2—\right]_n}$$

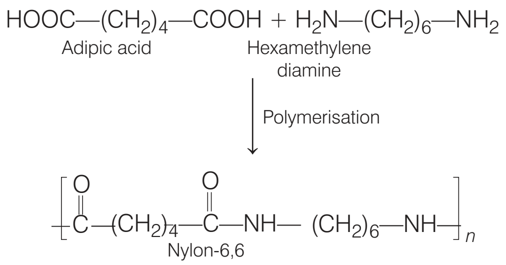
291. The monomer of polymer



$$\mathrm{—CH_2—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2—\overset{+}{C}\!\!<^{CH_3}_{CH_3}} \text{ is } \mathrm{CH_2=C\!<^{CH_3}_{CH_3}}$$

because 2-methylpropene shows cationic polymerisation.

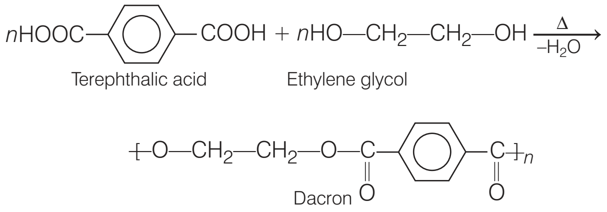
292. Nylon-6,6 polymer is formed as :



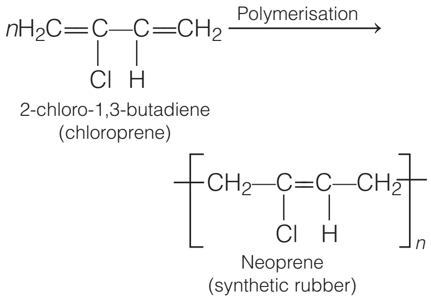
$$\underset{\text{Adipic acid}}{\mathrm{HOOC—(CH_2)_4—COOH}} + \underset{\text{Hexamethylene diamine}}{\mathrm{H_2N—(CH_2)_6—NH_2}} \xrightarrow{\text{Polymerisation}} \underset{\text{Nylon-6,6}}{\mathrm{\left[—\overset{\overset{O}{\|}}{C}—(CH_2)_4—\overset{\overset{O}{\|}}{C}—NH—(CH_2)_6—NH—\right]_n}}$$

Thus, option (d) is correct.

293. Dacron commonly known as terylene, is obtained by heating a mixture of terephthalic acid and ethylene glycol at 420-460 K. In the presence of zinc acetate and antimony trioxide as a catalyst.



294. Neoprene (synthetic rubber) is a polymer of chloroprene, i.e. 2-chloro-1, 3-butadiene.



$$nH_2C{=}\underset{Cl}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}{=}CH_2 \xrightarrow{\text{Polymerisation}} \left[-CH_2-\underset{Cl}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}-CH_2-\right]_n$$

2-chloro-1,3-butadiene (chloroprene)

Neoprene (synthetic rubber)

30. *Chemistry in Everyday Life*

295. Tranquilizers are the chemicals that reduce anxiety and mental diseases.Tranquilizer is the strain reliever also used for mild and essential component of sleeping pills. Thus, they are sometimes called psychotherapeutic drugs. Equanil, valium, serotonin and barbiturates (hypnotic) are some commonly used tranquilizers.

296. Diphenylhydramine (benadryl) is used as an antihistamine.

297. Novalgin (Dipyrone) is a non-narcotic analgesic used as pain reliever.

- Penicillin is an antibiotic used for curing rheumatic fever.
- Streptomycin is an antibiotic drug.
- Chloromycetin is an antibiotic drug.

298. Antiseptics and disinfectants both either kill or prevent the growth of microorganisms. The main point of difference between these two is that the former (antiseptics) are used for living beings whereas disinfectants are not safe for living tissues. These are actually used for inanimate objects like floors, tiles, etc.

A substance like phenol in its lower concentration (0.2%) behaves as antiseptic, whereas in higher concentration (1%) as disinfectant. Chlorine and iodine are strong disinfectants whereas dilute solutions of boric acid and hydrogen peroxide are mild antiseptics.

299. Aspartame is the only artificial sweetener which is stable at lower temperature and decomposes at higher temperature. It is also called ‘nutra sweet’. It’s relative sweetness value is 180 times sweetes than cane sugar.