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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / PMTs with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.10 M) which are to be separated by selective precipitation. Which one of these metals will get precipitated and what will be its percentage? (K_{sp} of AgI = 8.5×10^{-17} and K_{sp} of $Hg_2I_2 = 2.5 \times 10^{-26}$)
   (a) Hg, 99.83%   (b) Ag, 99.83%
   (c) Hg, 25.75%   (d) Ag, 25.75%

2. Traces of fluoride ions (F^-) in drinking water (about 1 ppm) greatly reduce the incidence of dental cavities (tooth decay). What is the reason for reduction in cavities?
   (a) The enamel $[3Ca_3(PO_4)_2 \cdot CaF_2]$ on the surface of teeth is converted to much harder $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$.
   (b) The enamel $[3Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ on the surface of teeth is converted to much harder $3Ca_3(PO_4)_2 \cdot CaF_2$.
   (c) The enamel $[Ca(OH)_2]$ on the surface of teeth is converted to CaF_2.
   (d) The enamel $[Ca_3(PO_4)_2 \cdot Ca(OH)_2]$ on the surface of teeth is converted to much harder $3Ca_3(PO_4)_2 \cdot CaF_6$.

3. Which of the given statements about N, O, P and Q with respect to M is not correct?
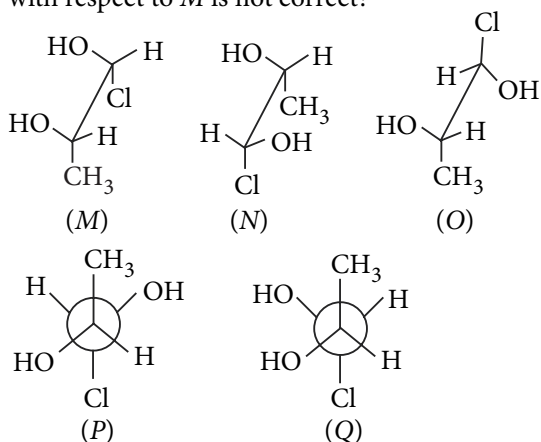
   (a) M and N are non-mirror image stereoisomers.
   (b) M and O are identical.
   (c) M and P are enantiomers.
   (d) M and Q are identical.

4. The ratio $[Ag^+]/[Ag(NH_3)_2]^+$ in 0.1 N NH_3 solution is (stability constant, K_f for $[Ag(NH_3)_2]^+ = 1.7 \times 10^7$)
   (a) 1.7×10^5 (b) 5.88×10^{-6}
   (c) 5.88×10^6 (d) 1.7×10^{-5}

5. A flask of 1 L having $NH_{3(g)}$ at 2.0 atm and 200 K is connected with another flask of volume 800 mL having $HCl_{(g)}$ at 8 atm and 200 K through a narrow tube of negligible volume. The two gases reacts to form $NH_4Cl_{(s)}$ with evolution of 43 kJ mol^{-1} heat. If heat capacity of $HCl_{(g)}$ at constant volume is 20 J K^{-1} mol^{-1} and neglecting heat capacity of flask, NH_4Cl and volume of solid NH_4Cl formed, calculate final temperature in flask.
   (Assume R = 0.08 L-atm K^{-1} mol^{-1})
   (a) 977.27 K   (b) 1177.27 K
   (c) 1077.27 K   (d) 1277.27 K

JEE ADVANCED

6. 1.8 g hydrogen atoms are excited by radiations. The study of spectra indicates that 27% of the atoms are in 3rd energy level, 15% of the atoms are in 2nd energy level and rest of the atoms are in the ground state. Ionisation potential of H is 13.6 eV. What will be the total energy involved when all the atoms return to ground state?
   (a) 265.7 kJ   (b) 566.8 kJ
   (c) 832.50 kJ   (d) 610.5 kJ

COMPREHENSION

Aldol condensation, Cannizzaro reaction, Claisen condensation, Claisen-Schmidt reaction are all similar in the sense that they involve nucleophilic attack at

carbonyl carbon. All these reactions are base catalysed. Hydroxides and alkoxides are the common bases that participate in the reactions. Except Cannizzaro reaction, all other reactions involve joining of two molecules and at least one of the reacting molecules is enolisable. Cannizzaro reaction, on the other hand, involves both non-enolisable compounds. In true sense, it is not a condensation reaction rather a disproportionation reaction. While both the compounds are enolisable in aldol condensation, only one is enolisable in Claisen-Schmidt condensation. In Claisen condensation, two ester molecules undergo condensation.

7. Identify the final product.

(a)

(b)

(c)
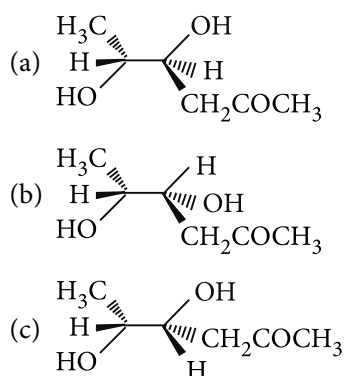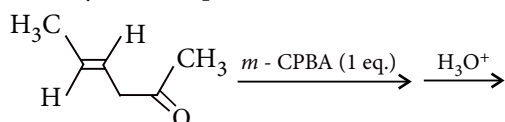
(d) None of the above

8. Pick the choice that contains the true statements.

I. MeO—⬡—CHO undergoes slow condensation than ⬡—CHO in Claisen-Schmidt condensation.

II. O_2N—⬡—CHO undergoes slow reaction than ⬡—CHO in Cannizzaro reaction.

III. H_5C_2O–CO–OC_2H_5 is more reactive than H–CO–OC_2H_5 in Claisen condensation.

(a) Only I and II   (b) Only II and III
(c) Only I and III   (d) All of these

INTEGER VALUE

9. The product R of the following nuclear change belongs to x^{th} group and y^{th} period of the periodic table :
$$_{88}Ra^{226} \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} P \xrightarrow{-\beta} Q \xrightarrow{-\alpha} R$$
Then, $x - y$ is
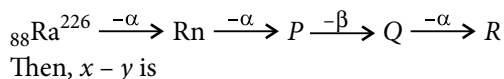
10. 0.22 g sample of a volatile compound, containing C, H and Cl only, on combustion gave 0.195 g CO_2 and 0.0804 g H_2O. 0.120 g of this compound occupies a volume of 37.24 mL at 105°C and 768 mm of pressure. The molecular formula of the compound is $C_aH_bCl_z$, The value of z is
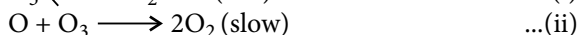
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Practice Paper 2017

Exam on 7th May

1. Which of the following ionic species has the greatest proton affinity to form stable compound?
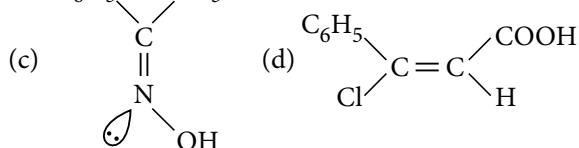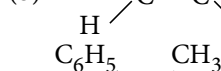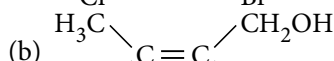   (a) I^- (b) HS^- (c) NH_2^- (d) F^-

2. The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows :
   $O_3 \rightleftharpoons O_2 + O$ (fast)   ...(i)
   $O + O_3 \longrightarrow 2O_2$ (slow)   ...(ii)
   The rate law expression should be
   (a) $r = k [O_3]^2$ (b) $r = k [O_3]^2 [O_2]^{-1}$
   (c) $r = k [O_3] [O_2]$ (d) unpredictable.

3. The *Z*-isomer among the following is

   (a)
   $$\begin{array}{c} H_3C \\ Cl \end{array} C = C \begin{array}{c} CH_2CH_3 \\ Br \end{array}$$

   (b)
   $$\begin{array}{c} H_3C \\ H \end{array} C = C \begin{array}{c} CH_2OH \\ CHO \end{array}$$

   (c)
   $$\begin{array}{c} C_6H_5 \quad CH_3 \\ C \\ \parallel \\ N \\ \quad OH \end{array}$$

   (d)
   $$\begin{array}{c} C_6H_5 \\ Cl \end{array} C = C \begin{array}{c} COOH \\ H \end{array}$$

4. Pick out the correct statements from the following :
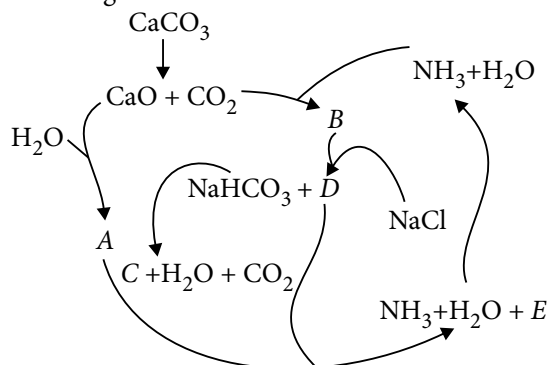   1. Cobalt (+3) is more stable in octahedral complexes.
   2. Zinc forms coloured ions or complexes.
   3. Most of the *d*-block elements and their compounds are ferromagnetic.
   4. Osmium shows +8 oxidation state.
   5. Cobalt (+2) is more stable in octahedral complexes.
   (a) 1 and 2   (b) 1 and 3
   (c) 2 and 4   (d) 1 and 4

5. The total kinetic energy of a sample of gas which contains N molecules at $-123°C$ is E_k joules. Another sample of gas at $27°C$ has total kinetic energy $2E_k$ joules. The number of molecules in the second sample of gas is
   (a) $N/2$ (b) $2N$ (c) N (d) N^2

6. The Solvay process can be represented by the following scheme :

   $$CaCO_3$$
   $$\downarrow$$
   $$CaO + CO_2 \quad\quad NH_3+H_2O$$
   $$H_2O \quad\quad\quad B$$
   $$NaHCO_3 + D$$
   $$A \quad\quad\quad NaCl$$
   $$C + H_2O + CO_2$$
   $$NH_3+H_2O + E$$

   Identify *A, B, C, D* and *E*.

	A	B	C	D	E
(a)	$Ca(OH)_2$	Na_2CO_3	$NaHCO_3$	NH_4Cl	$Ca(OH)_2$
(b)	$Ca(OH)_2$	NH_4HCO_3	$NaHCO_3$	$NaCl$	$CaCl_2$
(c)	$Ca(OH)_2$	$NaHCO_3$	Na_2CO_3	$NaCl$	$Ca(OH)_2$
(d)	$Ca(OH)_2$	NH_4HCO_3	Na_2CO_3	NH_4Cl	$CaCl_2$

7. Which of the following is aromatic?

   (a) [cyclohexane ring] (b) [cyclohexene ring] (c) [cyclopentadienyl cation] (d) [cycloheptatrienyl anion]
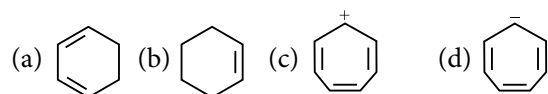
8. In view of the signs of $\Delta_r G°$ for the following reactions :
   $PbO_2 + Pb \longrightarrow 2PbO; \Delta_r G° < 0$
   $SnO_2 + Sn \longrightarrow 2SnO; \Delta_r G° > 0$
   Which oxidation states are more characteristic for lead and tin?
   (a) For lead + 2, for tin + 4
   (b) For lead + 4, for tin + 2
   (c) For lead + 2, for tin + 2
   (d) For lead + 4, for tin + 4
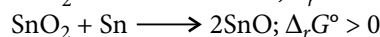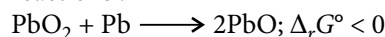
9. A crystal of lead (II) sulphide has NaCl structure. In this crystal the shortest distance between a Pb^{2+} ion and S^{2-} ion is 297 pm. What is the volume of the unit cell of lead sulphide?
   (a) $209 \cdot 6 \times 10^{-24}\,cm^3$ (b) $26 \cdot 2 \times 10^{-24}\,cm^3$
   (c) $52 \cdot 4 \times 10^{-24}\,cm^3$ (d) $104 \cdot 8 \times 10^{-24}\,cm^3$

10. One dm^3 solution containing 10^{-5} mole each of Cl^- ions and CrO_4^{2-} ions is treated with 10^{-4} mole of silver nitrate. Which of the following observations is correct?
    [K_{sp} of $Ag_2CrO_4 = 4 \times 10^{-12}$, K_{sp} of $AgCl = 1 \times 10^{-10}$]
    (a) Precipitation does not occur.
    (b) Only silver chromate gets precipitated.
    (c) Only silver chloride gets precipitated.
    (d) Both silver chromate and silver chloride start precipitating simultaneously.

11. During dialysis
    (a) only colloidal particles can diffuse through animal membrane
    (b) solvent molecules, ions and colloidal particles can diffuse through animal membrane
    (c) all kind of particles can diffuse through the animal membrane
    (d) only ions can diffuse through the animal membrane.

12. Which is the best behaviour of Br_2 in the reaction given below?
    $H_2O + Br_2 \longrightarrow HOBr + HBr$
    (a) Proton acceptor only
    (b) Both oxidising and reducing
    (c) Oxidising only
    (d) Reducing only

13. Arrange the following compounds in the increasing order of bond length of O — O bond :
    O_2, $O_2[AsF_6]$, KO_2
    (a) $O_2[AsF_6] < O_2 < KO_2$
    (b) $O_2[AsF_6] < KO_2 < O_2$
    (c) $O_2 < O_2[AsF_6] < KO_2$
    (d) $KO_2 < O_2 < O_2[AsF_6]$

14. Oxidation state of nitrogen is correctly given for

Compound	Oxidation state
(a) $[Co(NH_3)_5Cl]Cl_2$	0
(b) NH_2OH	+ 1
(c) $(N_2H_5)_2SO_4$	+ 2
(d) Mg_3N_2	– 3

15. A pure crystalline substance on heating first forms a turbid liquid at constant temperature and at higher temperature, turbidity completely disappears. The behaviour is a characteristic of substance forming
    (a) allotropic crystals (b) liquid crystals
    (c) isomeric crystals (d) isomorphous crystals.

16. Consider the following bond cleavages :
    $A.\ CH_3 - X \longrightarrow ;\quad B.\ CH_3 - X \longrightarrow ;\quad C.\ CH_3 - X \longrightarrow$
    Carbon species formed in *A, B* and *C* are respectively

	A	B	C
(a)	free radical	carbocation	carbanion
(b)	free radical	carbanion	carbocation
(c)	carbocation	carbanion	free radical
(d)	carbanion	carbocation	free radical

17. Two elements X (atomic weight = 75) and Y (atomic weight = 16) combine to give a compound having 75.8% X. The formula of the compound is
    (a) XY (b) X_2Y (c) X_2Y_2 (d) X_2Y_3

18. The standard reduction potentials for two reactions are given below :
    (i) $AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-_{(aq)}$; $E° = 0.22$ V
    (ii) $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E° = 0.80$ V
    The solubility product of AgCl under standard conditions of temperature (298 K) is
    (a) 1.6×10^{-5} (b) 1.5×10^{-8}
    (c) 3.2×10^{-10} (d) 1.5×10^{-10}

19. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. The ionisation energy of sodium in $kJ\ mol^{-1}$ is
    (a) 425 (b) 495 (c) 395 (d) 325

20. 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?
    (a) Galena (b) Copper pyrite
    (c) Sphalerite (d) Argentite

21. The density of a DNA sample is 1.1 g cm^{-3} and its molar mass determined by cryoscopic method is found to be 6.0×10^8 g mol^{-1}. What is the volume occupied by one DNA molecule?
    (a) $1.0 \times 10^{-15}\,cm^3$ (b) $2.0 \times 10^{-15}\,cm^3$
    (c) $3.0 \times 10^{-15}\,cm^3$ (d) $1.7 \times 10^{-23}\,cm^3$

22. α-Helical structure of a protein has
    (a) 3.8 α-amino acids per turn and a 15 membered ring
    (b) 3.8 α-amino acids per turn and a 13 membered ring

(c) 3.6 α-amino acids per turn and a 13 membered ring

(d) 3.6 α-amino acids per turn and a 15 membered ring.

23. A human body heats the surroundings at a rate of 200 W. The entropy change of surroundings contributed by the person in a day at 20°C is
(a) 58976 kJ/K
(b) 58.976 kJ/K
(c) 589.76 kJ/K
(d) 5897.6 J/K

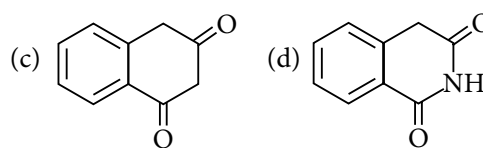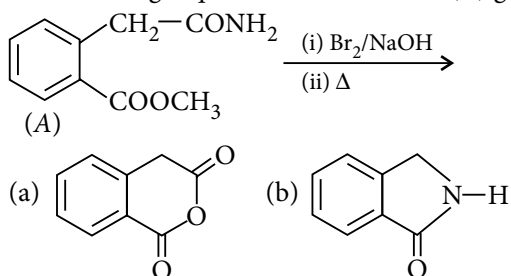**24.** Consider the following reactions :
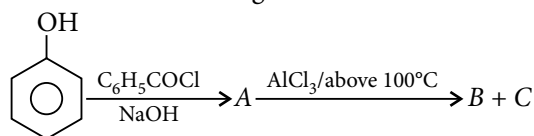
The major product (B) of the reaction is

(a)

(b)

(c)

(d)

25. Which among the following is the most important factor in making fluorine the strongest oxidising halogen?
(a) Electron affinity
(b) Bond dissociation energy
(c) Hydration enthalpy
(d) Ionisation enthalpy

26. The following sequence of reactions on (A) gives :

(a)

(b)

(c)

(d)

27. Which one of the following orbitals has orbital angular momentum equal to that of 2p-orbital?
(a) 3p
(b) 2d
(c) 3d
(d) 4s

28. A solution contains 0.8960 g of K_2SO_4 in 500 mL solution. Its osmotic pressure is found to be 0.690 atm at 27 °C. The value of van't Hoff factor is
(a) 0.36
(b) 2.72
(c) 2.11
(d) 0.47

29. The carbide which is used as abrasive is
(a) CaC_2
(b) Al_4C_3
(c) SiC
(d) all of these.

30. Which one of the following statements is true for protein synthesis (translation)?
(a) Amino acids are directly recognized by m-RNA.
(b) The third base of the codon is less specific.
(c) Only one codon codes for an amino acid.
(d) Every t-RNA molecule has more than one amino acid attachment.

31. 2.9 g of an unknown gas at 95 °C occupies the same volume as 0.184 g of dihydrogen at 17 °C and at the same pressure. What is the molar mass of the unknown gas?
(a) 40 g mol^{-1}
(b) 46 g mol^{-1}
(c) 50 g mol^{-1}
(d) 38 g mol^{-1}

32. The reaction of P_4 with X leads selectively to P_4O_6. Then, X is
(a) dry O_2
(b) a mixture of O_2 and N_2
(c) moist O_2
(d) O_2 in the presence of aqueous NaOH.

33. Element with which of the following electronic configurations will have the highest electron gain enthalpy?
(a) $[Ar]3d^{10}4s^24p^1$
(b) $[Ar]3d^{10}4s^24p^4$
(c) $[Ar]3d^{10}4s^24p^5$
(d) $[Ar]3d^{10}4s^24p^3$

34.
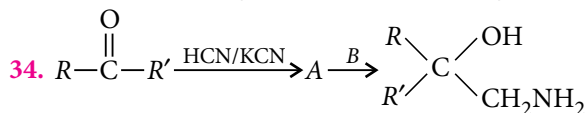
In the above sequence of reactions, A and B are

(a) A is $RR'C\overset{CN}{\underset{OH}{\diagdown}}$, B is $LiAlH_4$

(b) A is $RR'C\overset{OH}{\underset{COOH}{\diagdown}}$, B is NH_3

(c) A is $RR'C\diagup^{CN}_{\diagdown OH}$, B is H_3O^+

(d) A is $RR'CH_2CN$, B is NaOH.

35. Which of the following plots does not represent the behaviour of an ideal binary liquid solution of A and B?
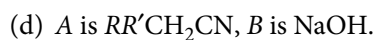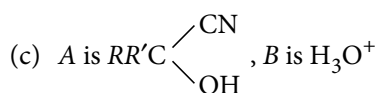(a) Plot of P_B versus X_B is linear.
(b) Plot of P_A versus X_A is linear.
(c) Plot of P_{Total} versus X_A or X_B is linear.
(d) Plot of P_{Total} versus X_A is non-linear.

36. A buffer solution is prepared in which the concentration of NH_3 is 0.3 M and the concentration of NH_4^+ is 0.2 M. If the equilibrium constant K_b for NH_3 equals 1.8×10^{-5}, what is the pH of this solution?
(a) 8.73   (b) 9.08   (c) 9.43   (d) 11.72

37. Cerium ($Z = 58$) is an important member of the lanthanoids. Which of the following statements about cerium is incorrect?
(a) The +4 oxidation state of cerium is not known in solutions.
(b) The +3 oxidation state of cerium is more stable than +4 oxidation state.
(c) The common oxidation states of cerium are +3 and +4.
(d) Cerium (IV) acts as an oxidising agent.

38. Negative soil pollution is
(a) reduction in soil productivity due to errosion and overuse
(b) reduction in soil productivity due to addition of pesticides and industrial wastes
(c) converting fertile land into barren land by dumping ash, sludge and garbage
(d) none of the above.

39. In the following sequence of reactions :
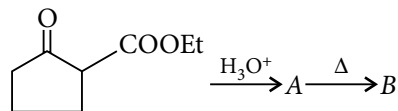
The compound B is
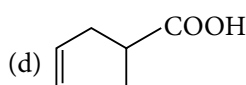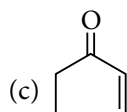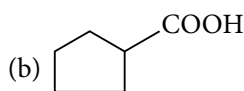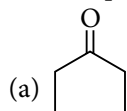
40. The number of chiral centres present in the following compound is
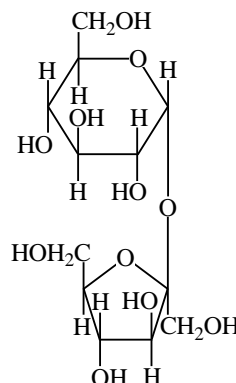
(a) 7
(b) 8
(c) 9
(d) 10

41. Which of the following compounds exhibits linkage isomerism?
(a) $[Co(en)_3]Cl_3$
(b) $[Co(NH_3)_6][Cr(en)_3]$
(c) $[Co(en)_2(NO_2)Cl]Br$
(d) $[Co(NH_3)_5Cl]Br_2$

42. The polymer given below is
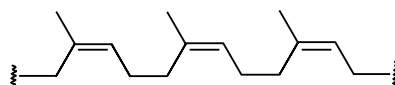
(a) natural rubber
(b) gutta percha
(c) neoprene
(d) polypropylene.

43. In which of the following molecules/ions, all the bonds are not equal?
(a) SF_4
(b) SiF_4
(c) XeF_4
(d) BF_4^-

44. Name the active chemotherapeutic agent present in brufen.
(a) 2-(p-Isobutylphenyl)propanoic acid
(b) Paracetamol
(c) Acetyl salicylic acid
(d) Methyl salicylate

45. Impure titanium is heated with iodine, titanium iodide is obtained which is removed and heated separately to get back titanium metal. What is this process called?
(a) Mond's process
(b) Mac Arthur Forest process
(c) van Arkel method
(d) Kroll process

SOLUTIONS

1. **(c) :** The conjugate acid of NH_2^- is NH_3, which is the weakest acid out of HI, H_2S and HF.

2. **(b) :** Rate depends upon slowest step.
Hence, from eq. (ii), $r = k [O_3] [O]$
From eq. (i),

$$K_{eq} = \frac{[O_2][O]}{[O_3]} \quad \text{or} \quad [O] = \frac{K_{eq} [O_3]}{[O_2]}$$

Hence, $r = k[O_3] \dfrac{K_{eq}[O_3]}{[O_2]} = k'[O_3]^2[O_2]^{-1}$

3. **(a)**

4. **(d) :** Co (+3) is more stable in octahedral complexes and osmium shows +8 oxidation state in its compounds *e.g.*, OsO_4.

5. **(c) :** $E_k = \dfrac{3}{2} \dfrac{N}{N_A} \times R \times 150 = 225 \dfrac{N}{N_A} \times R,$

Let number of molecules in the second sample of gas be N_x.

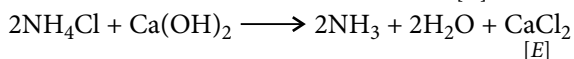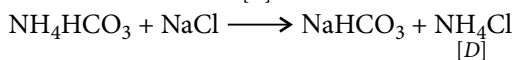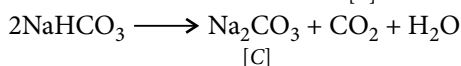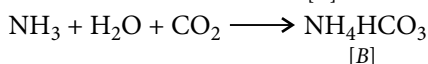$2E_k = \dfrac{3}{2} \dfrac{N_x}{N_A} R \times 300 = 450 \dfrac{N_x}{N_A} R$

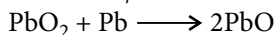$\therefore \quad 2 \times 225 \, NR = 450 \, N_x R \quad \text{or} \quad N_x = N$

6. **(d) :** $\underset{[A]}{CaO + H_2O \longrightarrow Ca(OH)_2}$

$\underset{[B]}{NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3}$

$\underset{[C]}{2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O}$

$\underset{[D]}{NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl}$

$\underset{[E]}{2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2}$

Thus, $A = Ca(OH)_2$; $B = NH_4HCO_3$; $C = Na_2CO_3$; $D = NH_4Cl$ and $E = CaCl_2$

7. **(c) :** A 6π electron system having conjugation is aromatic in nature.

8. **(a) :** Negative value of $\Delta_r G^\circ$ for the reaction,
$$PbO_2 + Pb \longrightarrow 2PbO$$
suggests that PbO (*i.e.*, oxidation state + 2) is more stable than +4. Similarly, we can say that Sn^{4+}, *i.e.*, oxidation state + 4 is more stable than +2 because the $\Delta_r G^\circ$ value for the reaction, $SnO_2 + Sn \longrightarrow 2SnO$, is positive. Thus, SnO_2 is more stable than SnO.

9. **(a) :** Edge, $a = 2 (r_+ + r_-) = 2 \times 297 \times 10^{-10}$ cm
$= 594 \times 10^{-10}$ cm
Volume $= a^3 = (594 \times 10^{-10} \text{ cm})^3$
$= 209{\cdot}6 \times 10^{-24} \text{ cm}^3$

10. **(c) :** Ionic product of AgCl = $[Ag^+] [Cl^-]$
$= 10^{-4} \times 10^{-5} = 10^{-9}$
Ionic product of $Ag_2CrO_4 = [Ag^+]^2 [CrO_4^{2-}]$
$= (10^{-4})^2 (10^{-5}) = 10^{-13}$
Ionic product of AgCl > K_{sp} of AgCl, hence, AgCl will precipitate out.
Ionic product of $Ag_2CrO_4 < K_{sp}$ for Ag_2CrO_4, hence, Ag_2CrO_4 will not precipitate out.

11. **(d)**
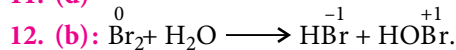
12. **(b) :** $\overset{0}{Br_2} + H_2O \longrightarrow \overset{-1}{H}\!Br + \overset{+1}{HO}Br.$
The oxidation state of Br_2 changes from 0 to –1 and 0 to +1. Hence, it acts as both oxidising as well as reducing agent.

13. **(a) :** O_2^+ ion is present in $O_2[AsF_6]$ and O_2^- ion is present in KO_2.
E.C. of $O_2 = KK\, \sigma(2s)^2 \, \sigma^*(2s)^2 \sigma(2p_z)^2$
$$\pi(2p_x)^2 = \pi(2p_y)^2 \pi^*(2p_x)^1 = \pi^*(2p_y)^1$$
Bond order $= \dfrac{8-4}{2} = 2$

E.C. of $O_2^+ = KK\, \sigma(2s)^2 \, \sigma^*(2s)^2 \sigma(2p_z)^2$
$$\pi(2p_x)^2 = \pi(2p_y)^2 \pi^*(2p_x)^1$$
Bond order $= \dfrac{8-3}{2} = 2.5$

E.C. of $O_2^- = KK\, \sigma(2s)^2 \, \sigma^*(2s)^2 \sigma(2p_z)^2$
$$\pi(2p_x)^2 = \pi(2p_y)^2 \pi^*(2p_x)^2 = \pi^*(2p_y)^1$$
Bond order $= \dfrac{8-5}{2} = 1.5$

Higher the bond order, smaller is the bond length. Hence, increasing order of O — O bond length is :
$O_2[AsF_6] < O_2 < KO_2$

14. **(d) :** (a) O.N. of N in NH_3 = – 3
(b) O.N. of N in NH_2OH
$= x +2 \times 1 - 2 + 1 = 0$ or $x = -1$
(c) O.N. of N in $(N_2H_5)_2^{2+}$
$= 2 \times (2x + 5) = +2$ or $x = -2$
(d) O.N. of N in Mg_3N_2
$= 3 \times (+ 2) + 2x = 0$ or $x = -3$

15. (b): Liquid crystals on heating first become turbid and then clear.

16. (a): A. $CH_3 \overset{\frown\frown}{—} X \xrightarrow[\text{fission}]{\text{Homolytic}} \dot{C}H_3 + \dot{X}$
<div align="center">Free radicals</div>

B. $CH_3 \overset{\frown}{—} X \xrightarrow[\text{fission}]{\text{Heterolytic}} \overset{+}{C}H_3 + X^-$
<div align="center">Carbocation</div>

C. $\overset{\frown}{C}H_3 — X \xrightarrow[\text{fission}]{\text{Heterolytic}} CH_3^- + X^+$
<div align="center">Carbanion</div>
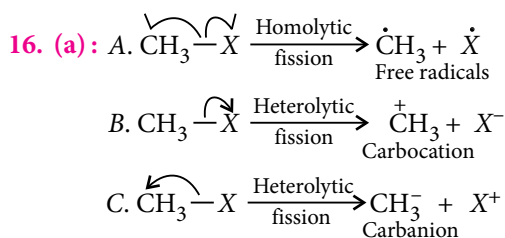
17. (d): $X:Y = \dfrac{75.8}{75} : \dfrac{24.2}{16} = 2:3$

∴ Empirical formula = X_2Y_3

18. (d): Subtracting eqn. (ii) from eqn (i),
$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$; $E° = -0.58$ V

$E = E° - \dfrac{0.059}{1} \log \dfrac{[Ag^+][Cl^-]}{[AgCl_{(s)}]}$

At equilibrium, $E = 0$ and $[AgCl_{(s)}] = 1$
∴ $E° = 0.059 \log [Ag^+][Cl^-] = 0.059 \log K_{sp}$
∴ $0.059 \log K_{sp} = -0.58$
   $\log K_{sp} = -9.831$
∴ $K_{sp} = 1.48 \times 10^{-10} \approx 1.5 \times 10^{-10}$

19. (b): Wavelength of the radiation,
$\lambda = 242$ nm $= 242 \times 10^{-9}$ m

Energy (per mole) of the photons $= \dfrac{N_A.hc}{\lambda}$

$= \dfrac{6.023 \times 10^{23}\,mol^{-1} \times 6.626 \times 10^{-34}\,J\,s \times 3 \times 10^8\,m\,s^{-1}}{242 \times 10^{-9}\,m}$

$= 4.95 \times 10^5$ J mol^{-1} = 495 kJ mol^{-1}

This energy is equal to the ionisation energy of sodium.

20. (d)

21. (a): Molar volume of DNA sample $= \dfrac{\text{Molar mass}}{\text{Density}}$

$= \dfrac{6 \times 10^8\,\text{g mol}^{-1}}{1.1\,\text{g cm}^{-3}} = 5.45 \times 10^8$ cm^3 mol^{-1}

∴ Volume of one DNA molecule

$= \dfrac{5.45 \times 10^8\,\text{cm}^3\text{mol}^{-1}}{6.022 \times 10^{23}\,\text{mol}^{-1}} = 0.9 \times 10^{-15}$ cm^3

$\approx 1.0 \times 10^{-15}$ cm^3

22. (c)

23. (b): As a human body heats the surrounding at a rate of 200 W (200 J/sec), then for one day
$q_{surr} = 86400 \times 200 = 17280000$ J

(∵ 1 day = 24 hr = 24 × 3600 sec = 86400 sec)

∴ $\Delta S_{surr} = \dfrac{q_{surr}}{T} = \dfrac{17280000}{293}$
    = 58976 J K^{-1} = 58.976 kJ K^{-1}

24. (c):
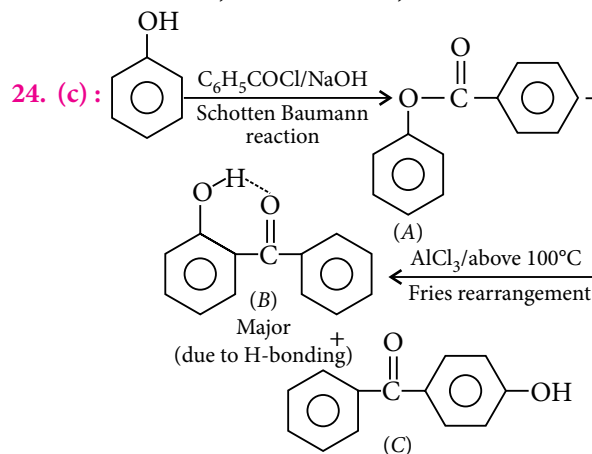
25. (c): F_2 has low bond dissociation energy (158.8 kJ mol^{-1}) and F^- has high hydration enthalpy (−515 kJ mol^{-1}) due to smaller size of F$^-$. And very large negative enthalpy of hydration for F$^-$ is the most important parameter in making fluorine the strongest oxidising agent.

26. (b):
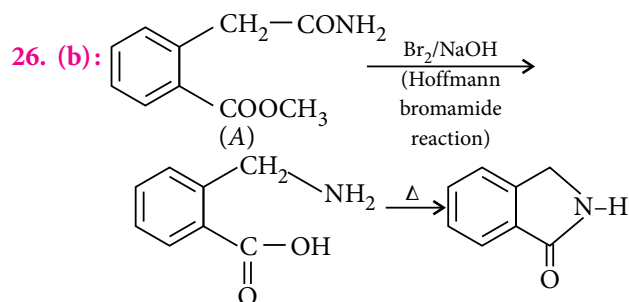
27. (a): Orbital angular momentum $= \sqrt{l(l+1)}\dfrac{h}{2\pi}$

$l = 1$, for p-orbitals. Thus, $3p$- and $2p$-orbitals will have same orbital angular momentum.

∴ Orbital angular momentum $= \sqrt{2}\dfrac{h}{2\pi}$

28. (b): Let us first calculate the observed molar mass,

$M_B = \dfrac{w_B \times R \times T}{\pi \times V}$

$w_B = 0.8960$ g, $V = 500$ mL = 0.5 L
$R = 0.082$ L atm mol^{-1} K^{-1}, $\pi = 0.690$ atm, $T = 300$ K

$M_B = \dfrac{0.8960 \times 0.082 \times 300}{0.690 \times 0.5} = 63.9$

Normal molar mass = 2 × 39 + 32 + 4 × 16 = 174
∴ van't Hoff factor,

$$i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{174}{63.9} = 2.72$$

29. (d)   **30. (b)**

31. (a): We know, $PV = \frac{w}{M}RT$

For unknown gas, $PV = \frac{2.9}{M} \times R \times 368$ ...(i)

For hydrogen, $PV = \frac{0.184}{2} \times R \times 290$ ...(ii)

From equations (i) and (ii),

$$\frac{2.9}{M} \times R \times 368 = \frac{0.184}{2} \times R \times 290$$
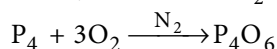
$$M = \frac{2.9 \times 368 \times 2}{0.184 \times 290} = 40\,\text{g mol}^{-1}$$

32. (b): P_4 gives P_4O_6 when oxygen is in limited supply. Hence, a mixture of O_2 and N_2 is most suitable.

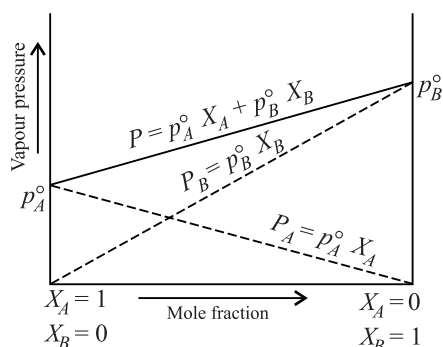$$P_4 + 3O_2 \xrightarrow{N_2} P_4O_6$$

33. (c): The element corresponding to configuration $[Ar]3d^{10}4s^24p^5$ will have the highest electron gain enthalpy due to the following reasons :
(i) Its size is the smallest amongst the given elements and nuclear charge is maximum.
(ii) After gaining one electron it acquires stable inert gas configuration.

34. (a)

35. (d): Plot of P_{Total} versus X_A or X_B is linear.

36. (c): $\text{pOH} = pK_b + \log \frac{[NH_4^+]}{[\text{base}]}$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.2}{0.3}\right) = 4.7447 + \log\left(\frac{2}{3}\right)$$

$$= 4.7447 - 0.1761 = 4.5686$$

$$\text{pH} = 14 - 4.5686 \approx 9.43$$

37. (a): Ce ($Z = 58$) can attain stable $4f^0$ configuration in +4 oxidation state and therefore, Ce can exhibit +4 oxidation state.

38. (a): Negative soil pollution is reduction in soil productivity due to errosion and overuse.

39. (a):
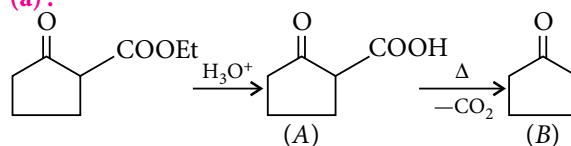
40. (c):
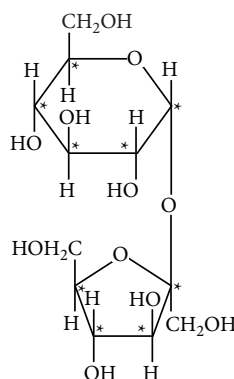
41. (c): This type of isomerism occurs in complex compounds which contain ambidentate ligands like NO_2^-, SCN^-, CN^-, $S_2O_3^{2-}$ and CO. These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

42. (a): Natural rubber is *cis* polymer.

43. (a): SF_4 molecule shows sp^3d hybridisation but its expected trigonal bipyramidal geometry gets distorted due to presence of a lone pair of electrons and it becomes distorted tetrahedral or see saw. Axial bonds suffer more repulsion than equatorial bonds hence, the bonds are not equivalent.
SiF_4 : sp^3 hybridisation and tetrahedral geometry.
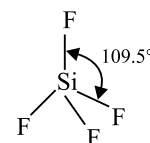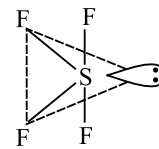
XeF_4 : sp^3d^2 hybridisation, shape is square planar instead of octahedral due to presence of two lone pairs of electrons on Xe atom.
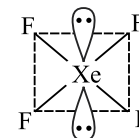
BF_4^- : sp^3 hybridisation and tetrahedral geometry.

44. (a)   **45. (c)**   ◈◈

JEE Advanced

Exam on 21st May

PRACTICE PAPER 2017

PAPER-I

SECTION 1 (MAXIMUM MARKS : 15)

- *This section contains FIVE questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.*
- *For each question, darken the bubble corresponding to the correct option in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

  Full Marks : +3 *If only the bubble corresponding to the correct option is darkened.*

  Zero Marks : 0 *If none of the bubbles is darkened.*

  Negative Marks : −1 *In all other cases.*

1. In the following process of disproportionation :

$$2ClO_3^- \rightleftharpoons ClO_2^- + ClO_4^-;$$

$\underset{\text{ion}}{\text{Chlorate}}$ $\underset{\text{ion}}{\text{Perchlorate}}$ $E^\circ_{ClO_4^-/ClO_3^-} = +0.36$ V,

$E^\circ_{ClO_3^-/ClO_2^-} = +0.33$ V

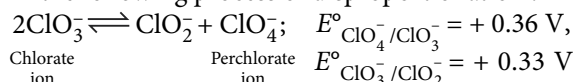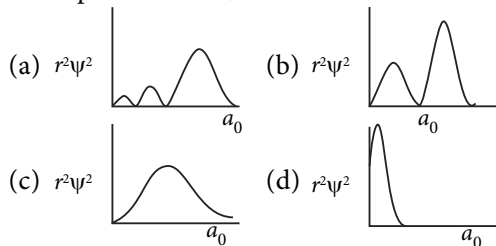Initial concentration of chlorate ion was 0.1 M. The equilibrium concentration of perchlorate ion will be

(a) 0.19 M (b) 0.1 M

(c) 0.024 M (d) 0.019 M

2. Which of the following alkenes is most reactive towards cationic polymerisation?

(a) $CH_2 = CHCH_3$ (b) $CH_2 = CHCl$

(c) $CH_2 = CHC_6H_5$ (d) $CH_2 = CHCO_2CH_3$

3. Which of the following radial distribution graphs correspond to $n = 3$, $l = 2$ for an atom?

4. Percentage ionisation of a weak acid can be calculated using the formula

(a) $100\sqrt{\dfrac{K_a}{C}}$ (b) $\dfrac{100}{1+10^{(pK_a-pH)}}$

(c) both (a) and (b) (d) none of these.

5. KI (excess) is added to the following solutions separately :

(I) $CuSO_4$ (II) $HgCl_2$ (III) $Pb(NO_3)_2$

The correct observation is

(a) a white precipitate of Cu_2I_2 in (I), an orange precipitate of HgI_2 in (II) which further dissolves and a yellow precipitate of PbI_2 in (III) are formed

(b) white precipitates of Cu_2I_2, HgI_2 and PbI_2 are formed respectively

(c) yellow precipitate in each case is formed

(d) a white precipitate of Cu_2I_2 in (I), an orange precipitate of K_2HgI_4 in (II) and a yellow precipitate of PbI_2 in (III) are formed.

SECTION 2 (MAXIMUM MARKS : 32)

- *This section contains EIGHT questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct.*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

  Full Marks : +4 *If only the bubble(s) corresponding to the correct option(s) is(are) darkened.*

  Partial Marks : +1 *For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.*

  Zero Marks : 0 *If none of the bubbles is darkened.*

  Negative Marks : −2 *In all other cases.*

- *For example, if (a), (c) and (d) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (a) and (d) will result in +2 marks; and darkening (a) and (b) will result in −2 marks, as a wrong option is also darkened.*

6. Benzaldehyde is reacted with alcoholic KCN in hot condition to get a product (*P*), which is subsequently applied to some other reactions. Each such reaction and respective products are shown in the given options. The incorrect reaction(s) is/are

(a) $P \xrightarrow{\text{dil. HNO}_3} \xrightarrow{OH^-}$

(b) $P \xrightarrow[C_2H_5OH]{\text{Na-Hg}}$

(c) $P \xrightarrow{OH^-}$

(d) $P \xrightarrow[\text{HCl}]{\text{Zn-Hg}} \xrightarrow{\Delta}$

7. $C_6H_5CH_2I \xrightarrow[\Delta]{NaN_3}$ Products

If reaction is assumed to involve nitrene as the intermediate, then possible product(s) is/are

(a) $C_6H_5CH_2NH_2$ (b) $C_6H_5N=CH_2$

(c) $C_6H_5NH_2$ (d) $C_6H_5CH \overset{||}{\underset{N}{N}}$

8. In which of the following pairs both the complexes show optical isomerism?

(a) cis-$[Cr(C_2O_4)_2Cl_2]^{3-}$, cis-$[Co(NH_3)_4Cl_2]$

(b) $[PtCl(dien)]Cl$, $[NiCl_2Br_2]^{2-}$

(c) $[Co(NO_3)_3(NH_3)_3]$, cis-$[Pt(en)_2Cl_2]$

(d) $[Co(en)_3]Cl_3$, cis-$[Co(en)_2Cl_2]Cl$
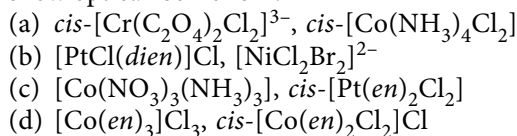
9. Which of the following products is/are incorrectly shown?

(a)

(b) $R-\overset{O}{\overset{||}{C}}-H \xrightarrow{CH_2N_2} R-CH-CH_2$ (Major product)

(c) $Ph-\overset{H}{\underset{|}{C}}=O \xrightarrow[\text{alcohol, }\Delta]{KCN} Ph-\overset{O}{\overset{||}{C}}-\overset{OH}{\overset{|}{C}}-H$ (Ph)

(d)
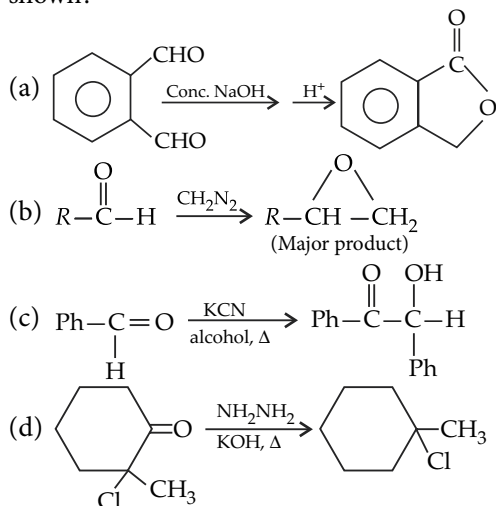
10. Which of the following statements is/are correct?

(a) A NaCl type AB-crystal lattice can be interpreted to be made up of two individual fcc unit cells of A^+ and B^- fused together in such a manner that the corner of one unit cell becomes the edge centre of the other.

(b) In a face-centred cubic unit cell, the body centre is an octahedral void.

(c) In fcc unit cell, octahedral and tetrahedral voids are equal.

(d) Tetrahedral voids = 2 × octahedral voids, is true for only ccp and hcp.

11. The correct statements about the given compound is/are
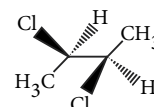
(a) compound is optically active

(b) compound possesses center of symmetry

(c) compound possesses plane of symmetry

(d) compound possesses axis of symmetry.

12. The given graphs I, II, III and IV represent general trends observed for different physisorption and chemisorption processes under mild conditions of temperature and pressure.
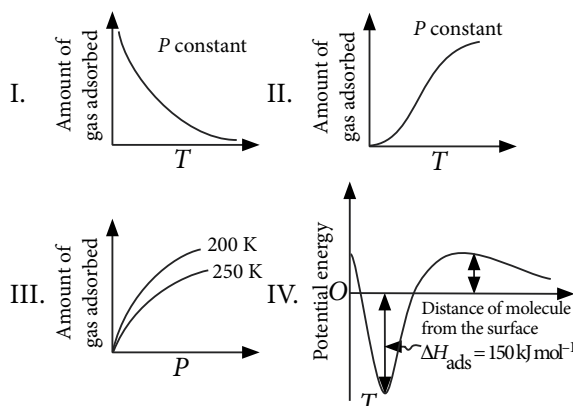
Which of the following options about I, II, III and IV is/are correct ?

(a) I is physisorption and II is chemisorption.

(b) I is physisorption and III is chemisorption.

(c) II and IV both represent chemisorption.

(d) IV and III both represent chemisorption.

13. Which of the given methods produce Cl_2?

(a) Electrolysis of brine

(b) Deacon process

(c) Heating MnO_2 with conc. HCl

(d) Heating KCl with conc. H_2SO_4

SECTION 3 (MAXIMUM MARKS : 15)

- *This section contains FIVE questions.*
- *The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive.*
- *For each question, darken the bubble corresponding to the correct integer in the ORS.*
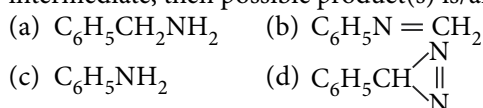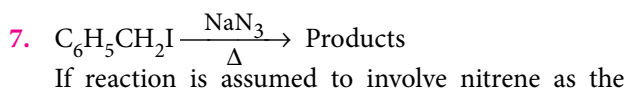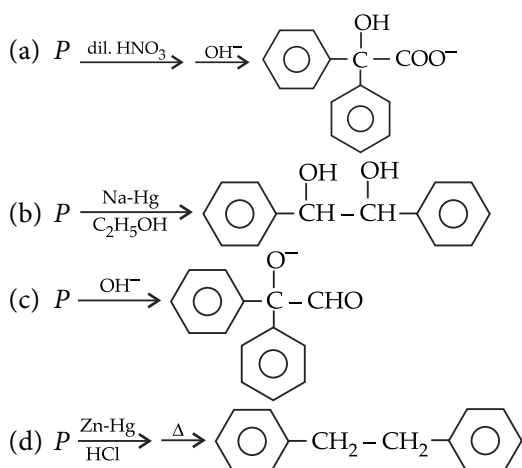- *For each question, marks will be awarded in one of the following categories :*

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Full Marks : *+3 If only the bubble corresponding to the correct answer is darkened.*
Zero Marks : *0 In all other cases.*

14. Which —COOH group is lost due to heating ?
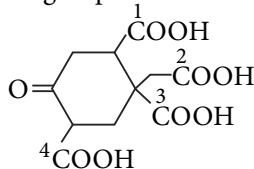
15. How many of the following compounds do not give NO_2 and O_2 simultaneously on heating at low temperature?
$Pb(NO_3)_2, NaNO_3, NH_4NO_3, NH_4NO_2, Mn(NO_3)_2, CsNO_3$

16. Number of hydrogen ions, a single molecule of the following species will lose on treatment with excess of NaOH is
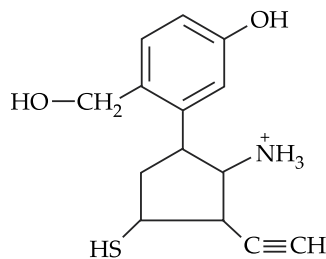
17. $^7_4$Be captures a *K*-electron into its nucleus. What will be the mass number of resulting nuclide?

18. In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm of Hg and, in 147 seconds, when initial pressure was 288 mm of Hg. Then the order of the reaction is

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PAPER-II

SECTION 1 (MAXIMUM MARKS : 18)

- *This section contains SIX questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.*
- *For each question, darken the bubble corresponding to the correct option in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*
  Full Marks : *+3 If only the bubble corresponding to the correct option is darkened.*
  Zero Marks : *0 If none of the bubbles is darkened.*
  Negative Marks : *–1 In all other cases.*

1. For the reaction : $Zn + Cu^{2+}_{(aq)} \rightleftharpoons Cu + Zn^{2+}_{(aq)}$

reaction quotient, $Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$.

Variation of E°_{cell} with log Q is of the type with $OA = 1.10$ V, E_{cell} will be 1.1591 V when
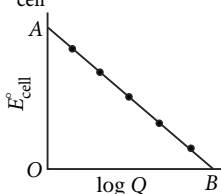
(a) $[Cu^{++}]/[Zn^{++}] = 0.1$
(b) $[Cu^{++}]/[Zn^{++}] = 0.01$
(c) $[Zn^{++}]/[Cu^{++}] = 0.01$
(d) $[Zn^{++}]/[Cu^{++}] = 0.1$

2. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of the solution required 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. The amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution respectively are
(a) 5.3 g, 4.2 g   (b) 0.053 g, 0.042 g
(c) 0.053 g, 4.2 g   (d) 0.42 g, 0.53 g

3. The van der Waals parameters *a* and *b* for two gases are given as :

Gas *A*	Gas *B*
$a = 6.5$ dm^6 bar/mole^2	$a = 18.0$ dm^6 bar/mole^2
$b = 0.056$ dm^3 mole	$b = 0.011$ dm^3 mole

Which of the following is/are correct?
(I) $(V_c)_A > (V_c)_B$ (II) $(P_c)_A > (P_c)_B$
(III)$(T_c)_A > (T_c)_B$
(a) I only   (b) I and II only
(c) I, II and III   (d) II and III only

4. Identify the product (*P*) in the following reaction.
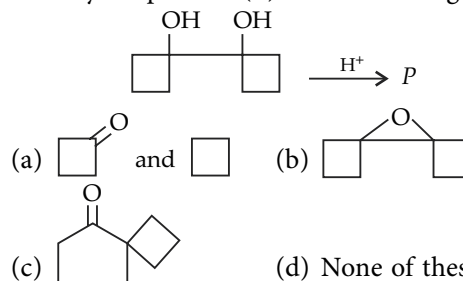
5. The major product formed in the following reaction is

(a)

(b)

(c)

(d)

6. A schematic plot of $\ln K_{eq}$ versus inverse of temperature for a reaction is shown in the figure. The reaction must be

(a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature.

SECTION 2 (MAXIMUM MARKS : 32)

- *This section contains EIGHT questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct.*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*
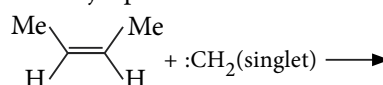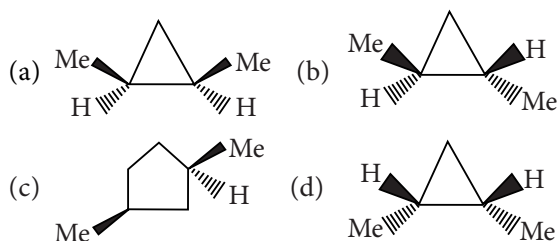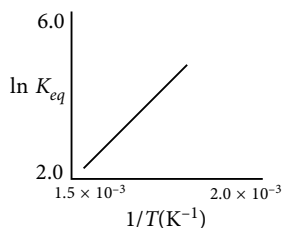 **Full Marks :** *+4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened.*
 **Partial Marks :** *+1 For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.*
  Zero Marks : *0 If none of the bubbles is darkened.*
  Negative Marks : *–2 In all other cases.*
- *For example, if (a), (c) and (d) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (a) and (d) will result in +2 marks; and darkening (a) and (b) will result in –2 marks, as a wrong option is also darkened.*

7. Which of the following carbohydrates is/are D-isomer(s)?

(a)

(b)

(c)

(d)
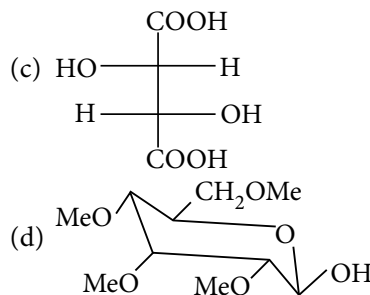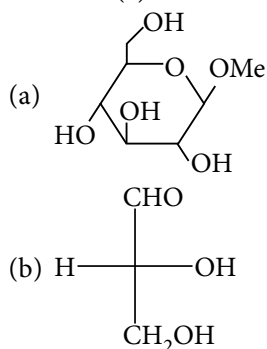
8. Reactant P gives product Q and/or R,
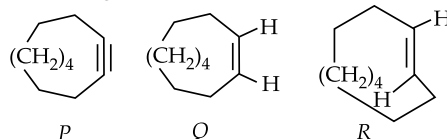
The possible reagents are :
(I) 2Na/liq. NH_3,
(II) H_2/Pd/$CaCO_3$ (quinoline)
(III) $2H_2$/Pd/C

The correct statement(s) with respect to the conversions is/are
(a) Q is obtained on treatment with reagent (I)
(b) R and Q are obtained on treatment with reagent (III)
(c) R is obtained on treatment with reagent (II)
(d) R is obtained on treatment with reagent (I).

9. When phenol is treated with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is formed. Which of the following species is/are involved in the above mentioned reaction as intermediate(s)?

(a)

(b)

(c)

(d)
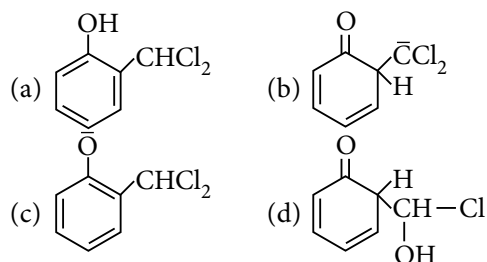
10. The total vapour pressure of a binary solution ($n_A = n_B$) is given by $P = (110x_A + 125x_B)$ mm Hg where x_A and x_B are the mole fractions of components A and B, respectively. It suggests that
(a) the vapour pressure of solution is less than that of the pure component B
(b) the vapour pressure of solution is more than that of pure component A
(c) vapour pressure of pure component A is 110 mm Hg and that of pure component B is 125 mm Hg
(d) vapour pressures of pure components A and B are 125 mm Hg and 110 mm Hg, respectively.

11. Which of the following reactions represent major products?

(a)

(b)

(c) $Ph - \overset{\overset{O}{\|}}{C} - NH_2 \xrightarrow{Br_2 + KOH} Ph - NH_2$

(d)
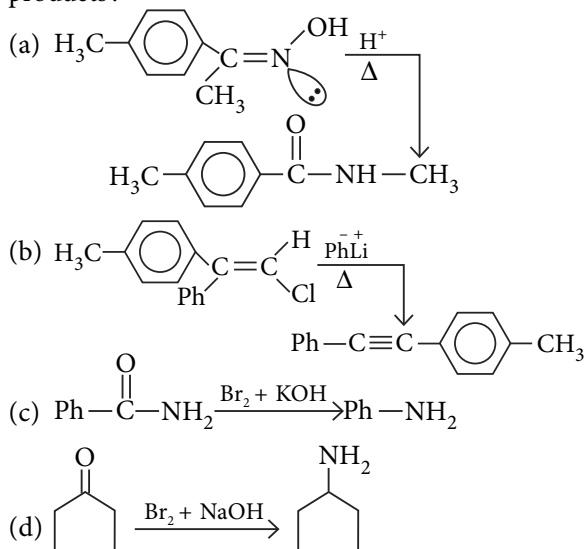
12. Which of the following properties is/are related to solution of rosy red complex of Ni^{2+} and dimethylglyoximate ligand?

(a) Geometry around Ni is square planar and diamagnetic in nature.

(b) Complex is stabilised by internal hydrogen bonding.

(c) It is an organometallic complex.

(d) Five membered chelate ring is formed when each molecule of dimethylglyoximate is bonded with metal ion.

13. Few reactions along with their names are given. Find the incorrect one(s) either with respect to name or product.

(a)
(Sommelet reaction)

(b) $CH_3 - \overset{\overset{O}{\|}}{C} - CH = \overset{+}{N} = \overset{-}{N} \xrightarrow[\text{(inert solvent)}]{Ag_2O \; \Delta} CH_2 = C = O$
(Wolff rearrangement)

(c)
(Schotten-Baumann reaction)

(d)
(Hoffmann rearrangement)

14. Consider the following compounds :

Pyrrole (I)   Pyridine (II)   NH$_2$
Aniline (III)

Which of the following statements is/are correct?

(a) I is more basic than II.

(b) II is more basic than I and III.

(c) III is more basic than II.

(d) I is weakly acidic.

SECTION 3 (MAXIMUM MARKS : 12)

- *This section contains TWO paragraphs.*
- *Based on each paragraph, there are TWO questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.*
- *For each question, darken the bubble corresponding to the correct option in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

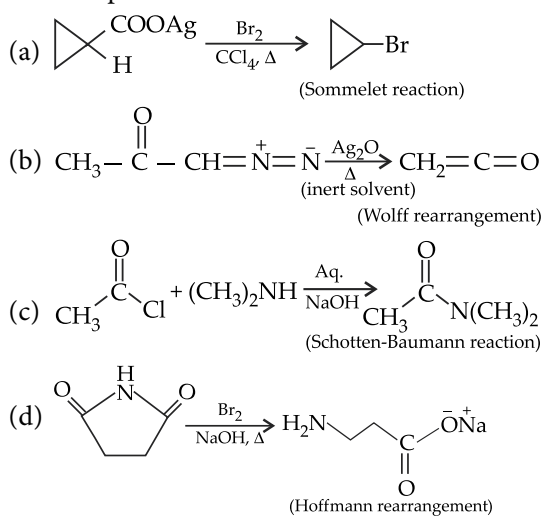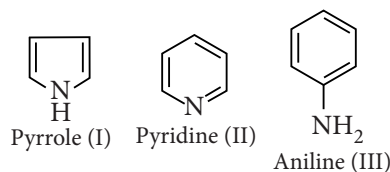 **Full Marks :** *+3 If only the bubble corresponding to the correct option is darkened.*

  Zero Marks : *0 In all other cases.*

PARAGRAPH 1

Boron forms a number of hydrides having the general formula B_nH_{n+4} and B_nH_{n+6}. These hydrides are called boranes. The simplest hydride of boron is diborane, B_2H_6. Boranes contain special types of bonds known as multicentre bonds. Boranes have high heat of combustion.

15. Three centre two electron bond is present in

(a) BF_3 (b) H_3BO_3

(c) B_2H_6 (d) none of these.

16. Which of the following is electron deficient compound?

(a) C_2H_6 (b) SiH_4

(c) PH_3 (d) B_4H_{10}

PARAGRAPH 2

Alcohols are converted to tosylates by treatment with *p*-toluene sulphonyl chloride (TsCl) in the presence of pyridine. This overall process converts a poor leaving group ($\bar{O}H$) into good one ($\bar{O}Ts$). A tosylate is a good leaving group because its conjugate acid *p*-toluene sulphonic acid is a strong acid.

Because alkyl tosylates have good leaving groups, they undergo both nucleophilic substitution and β-elimination.

17. Find the major product of following reaction :

(a)

(b) $CH_3-CH=C{\atop}\begin{matrix}H\\CH_3\end{matrix}$

(c)

(d)
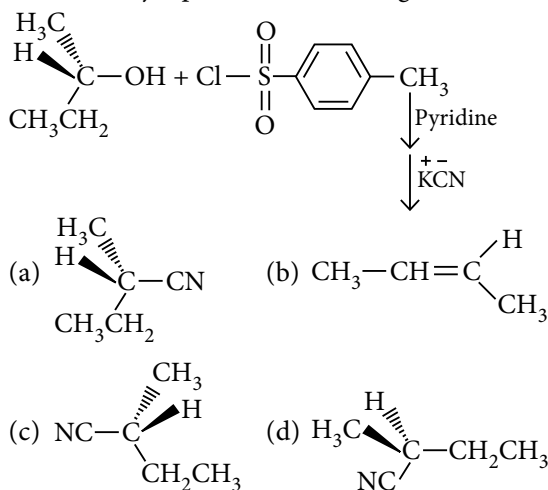
18. Identify the final product of following sequence of reactions :

(a)

(b)

(c)

(d)

SOLUTIONS

PAPER-I

1. (d) :
$$ClO_{3(aq)}^- + H_2O_{(l)} \rightarrow ClO_{4(aq)}^- + 2H_{(aq)}^+ + 2e^-$$
$$\underline{2H_{(aq)}^+ + ClO_{3(aq)}^- + 2e^- \rightarrow ClO_{2(aq)}^- + H_2O_{(l)}}$$
$$2ClO_{3(aq)}^- \rightleftharpoons ClO_{2(aq)}^- + ClO_{4(aq)}^-$$

$E^\circ_{cell} = E^\circ_{ClO_3^-/ClO_2^-} - E^\circ_{ClO_4^-/ClO_3^-}$
$E^\circ_{cell} = 0.33 - 0.36 = -0.03$ V

$E_{cell} = E^\circ_{cell} - \dfrac{0.059}{n}\log Q$

At equilibrium, $E_{cell} = 0$, $n = 2$, $Q = K$

$0 = -0.03 - \dfrac{0.059}{2}\log K$

$\log K = \dfrac{-0.06}{0.059}$

$\log K = -1$, ∴ $K = \dfrac{1}{10}$

$$2ClO_{3(aq)}^- \rightleftharpoons ClO_{2(aq)}^- + ClO_{4(aq)}^-$$

Initial conc. :   0.1   0   0
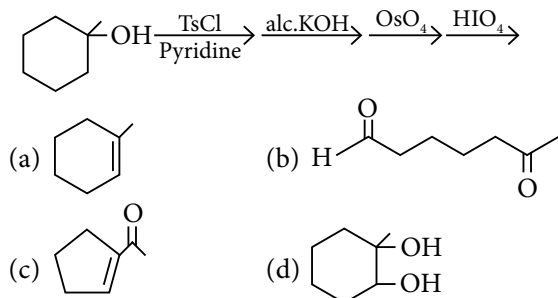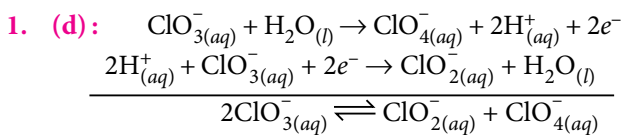At equil. :   0.1–2x   x   x

$K = \dfrac{x \times x}{(0.1-2x)^2} = \dfrac{1}{10}$ ⟹ $10x^2 = (0.1-2x)^2$

⟹ $x = 0.019$ M

2. (c) : In cationic polymerisation, carbocations are formed. Greater the stability of the carbocation, more reactive is the alkene. The stability of intermediate carbocations follows the order :

$CH_3-\overset{+}{C}HC_6H_5 > CH_3-\overset{+}{C}HCH_3 >$

$CH_3-\overset{+}{C}H-Cl > CH_3-\overset{+}{C}HCO_2CH_3$
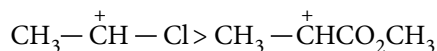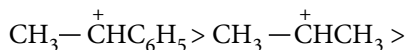
Therefore, reactivity decreases in the same order and styrene is the most reactive.

3. (c)

4. (c) : For a weak acid dissociation equilibria, degree of dissociation, α is given as :

$\alpha = \sqrt{\dfrac{K_a}{C}}$ ∴   % $\alpha = 100\sqrt{\dfrac{K_a}{C}}$

Also, $K_a = \dfrac{[H^+][A^-]}{[HA]} = \dfrac{[H^+].C\alpha}{C(1-\alpha)} = \dfrac{[H^+].\alpha}{(1-\alpha)}$

$\log K_a = \log[H^+] + \log\dfrac{\alpha}{(1-\alpha)}$

or $pK_a = pH + \log\dfrac{(1-\alpha)}{\alpha}$

or $pK_a - pH = \log\dfrac{(1-\alpha)}{\alpha}$

∴ $\dfrac{1-\alpha}{\alpha} = 10^{pK_a-pH}$ or $\dfrac{1}{\alpha} = 10^{pK_a-pH}+1$

or $\alpha = \dfrac{1}{(1+10^{pK_a-pH})}$ ⟹ % $\alpha = \dfrac{100}{1+10^{(pK_a-pH)}}$

5. (a) : $2CuSO_4 + 4KI \longrightarrow \underset{\text{White ppt.}}{Cu_2I_2} + 2K_2SO_4 + I_2$

$HgCl_2 + 2KI \longrightarrow \underset{\text{Orange ppt.}}{HgI_2} + 2KCl$

$HgI_2 + 2KI \longrightarrow \underset{\text{Soluble}}{K_2HgI_4}$

$Pb(NO_3)_2 + 2KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2} + 2KNO_3$
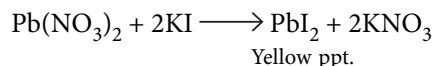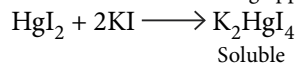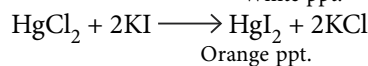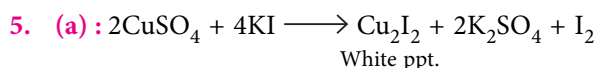
6. (c, d) : The given reaction is benzoin condensation to give benzoin (P) which can undergo reactions given in (a) and (b).

(a)

(b)

7. (b) :
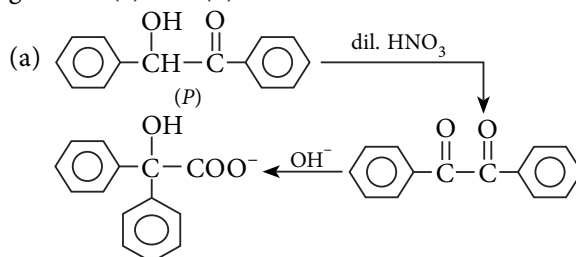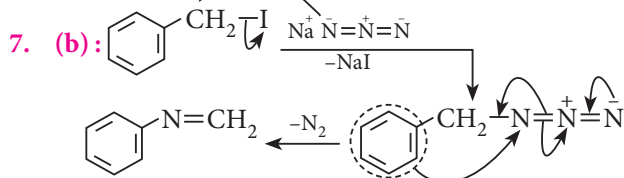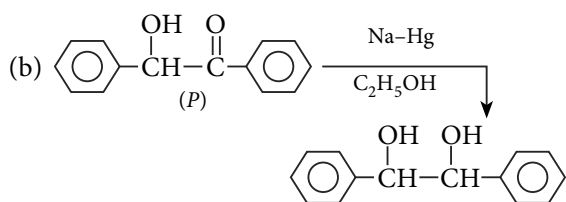
8. (d) : Optical isomerism is shown by octahedral complexes of the type $[M(AA)_2X_2]$ and $[M(AA)_3]$.

$[Co(en)_3]Cl_3$ *i.e.,* $[Co(en)_3]^{3+}$

Mirror
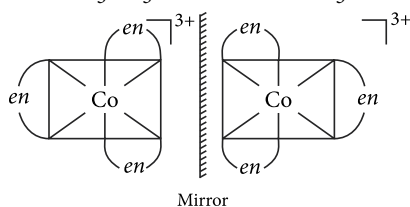
cis-$[Co(en)_2Cl_2]Cl$ *i.e.,* cis-$[Co(en)_2Cl_2]^+$

Mirror

9. (d) : (a)

(b)
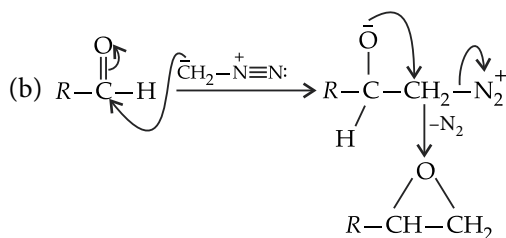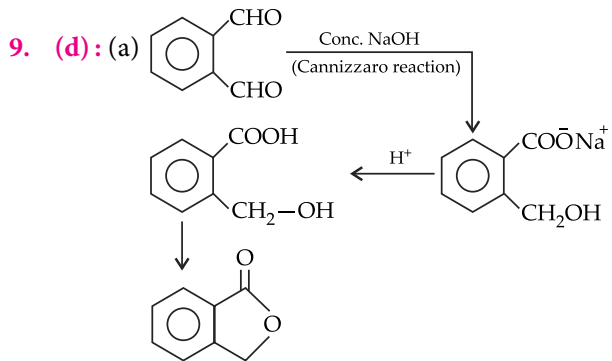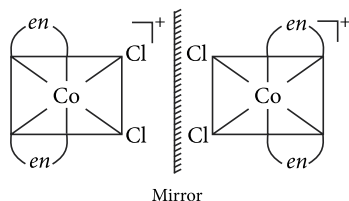
(c) This is benzoin condensation.

(d)
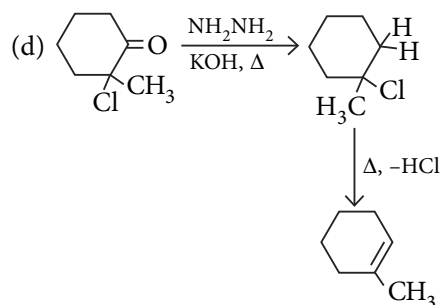
10. (a,b,d)   **11. (a,d)**

12. (a,c) : In graph I, the amount of adsorption decreases with increase of temperature and in group III, the amount of adsorption increases with increase of pressure. Hence, they represent physisorption.
In graph II, amount of adsorption increases with increase of temperature. Hence, it represents chemisorption. Graph IV shows the formation of a chemical bond hence, it represents chemisorption.

13. (a,b,c) : Electrolysis of brine ;
$$2NaCl + 2H_2O \longrightarrow Cl_2 + H_2 + 2NaOH$$
Deacon process ; $2HCl + \dfrac{1}{2}O_2 \xrightarrow{CuCl_2} Cl_2 + H_2O$

$$MnO_2 + 4HCl \underset{\text{(conc.)}}{\xrightarrow{\Delta}} MnCl_2 + Cl_2 + 2H_2O$$

$$2KCl + H_2SO_4 \underset{\text{(conc.)}}{\longrightarrow} 2HCl + K_2SO_4$$
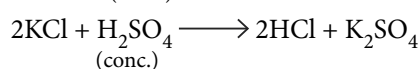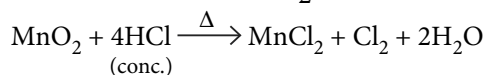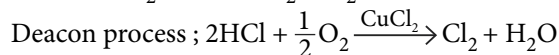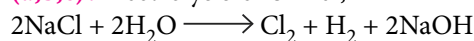
14. (4) :
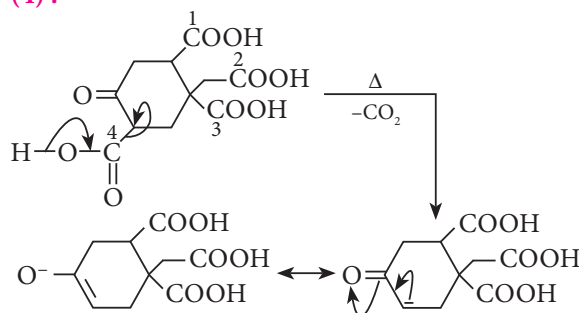
On heating, CO_2 molecule is removed, from that site where anion is resonance stabilised. Hence, CO_2 from $-\overset{4}{C}OOH$ is lost readily after heating.

15. (5) : $2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2$

$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$Mn(NO_3)_2 \xrightarrow{\Delta} MnO_2 + 2NO_2$

$CsNO_3 \xrightarrow{\Delta} CsNO_2 + \dfrac{1}{2}O_2$
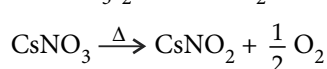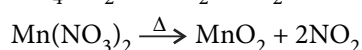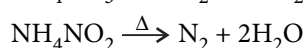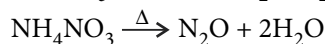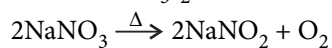
16. (3) :
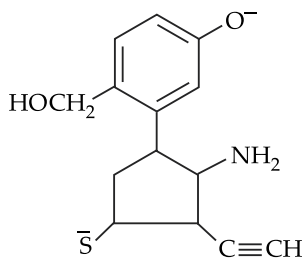
H_2O is a stronger acid than $RC \equiv CH$ and RCH_2OH. Thermodynamics supports the formation of weaker acid.

17. (7) : In K-electron capture, a proton of nucleus changes into a neutron and a neutrino is emitted.

$$_{1}^{1}H + _{-1}^{0}e \longrightarrow _{0}^{1}n + v$$
$$_{4}^{7}Be + _{-1}^{0}e \longrightarrow _{3}^{7}Li + v$$
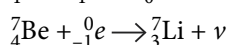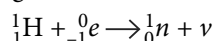
18. (3) : $\dfrac{t_2}{t_1} = \left(\dfrac{A_1}{A_2}\right)^{n-1}$

where, t_1 and t_2 represent time in seconds, A_1 and A_2 are pressures in mm of Hg.

$$\Rightarrow n = 1 + \dfrac{\log\left[\dfrac{t_2}{t_1}\right]}{\log\left[\dfrac{A_1}{A_2}\right]} = 1 + \dfrac{\log\left[\dfrac{147}{108}\right]}{\log\left[\dfrac{336}{288}\right]}$$

$$= 1 + \dfrac{0.1339}{0.0669} = 1 + 2 = 3$$

PAPER-II

1. (c) : $E_{cell} = E_{cell}^{\circ} - \dfrac{0.0591}{2}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

From the given plot, $OA = E_{cell}^{\circ} = 1.10$ V

$$1.1591 = 1.10 - \dfrac{0.0591}{2}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$$

$\therefore \log\dfrac{[Zn^{2+}]}{[Cu^{2+}]} = -2$

Taking antilog, $[Zn^{2+}]/[Cu^{2+}] = 0.01$

2. (a) : meq. of H_2SO_4 used for 10 mL mixture using phenolphthalein indicator = $2.5 \times 0.1 \times 2 = 0.5$

$\therefore \dfrac{1}{2} \times$ meq. of $Na_2CO_3 = 0.5$ ...(i)

Now, methyl orange is added in this solution after 1st end point.

meq. of H_2SO_4 used for solution after 1st end point using methyl orange indicator = $2.5 \times 0.2 \times 2 = 1$

$\therefore \dfrac{1}{2}$ meq. of Na_2CO_3 + meq. of $NaHCO_3 = 1$ ...(ii)

From equations (i) and (ii),
meq. of $NaHCO_3 = 0.5$, meq. of $Na_2CO_3 = 1.0$
Let 'x' g of Na_2CO_3 and 'y' g of $NaHCO_3$ be present per 10 mL of solution.

$\therefore \dfrac{x}{106/2} \times 1000 = 1$

$\therefore x = 0.053$ g/10 mL

Strength of $Na_2CO_3 = \dfrac{0.053 \times 1000}{10} = 5.3$ g L^{-1}

Also, $\dfrac{y}{84} \times 1000 = 0.5$

$y = 0.042$ g/10 mL

Strength of $NaHCO_3 = \dfrac{0.042 \times 1000}{10} = 4.2$ g L^{-1}

3. (a) : $V_c = 3b$

$\because (b)_A > (b)_B$ $\therefore (V_c)_A > (V_c)_B$

$P_c = \dfrac{a}{27b^2}$

$(P_c)_A = \dfrac{6.5}{27 \times (0.056)^2} = 76.76$

$(P_c)_B = \dfrac{18}{27 \times (0.011)^2} = 5509.6$

$\therefore (P_c)_B > (P_c)_A$

$T_c = \dfrac{8a}{27Rb}$

$(T_c)_A = \dfrac{8 \times 6.5}{27 \times 0.0821 \times 0.056} = 418.9$

$(T_c)_B = \dfrac{8 \times 18}{27 \times 0.0821 \times 0.011} = 5905.5$

$\therefore (T_c)_B > (T_c)_A$

4. (c) :

5. (a) :

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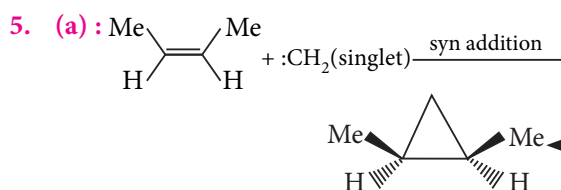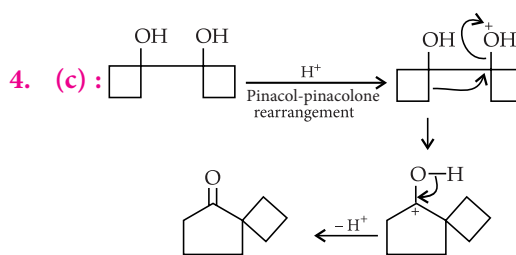
6. (a) : $\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H}{R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

$\ln \dfrac{6}{2} = \dfrac{\Delta H}{R}[1.5\times10^{-3} - 2\times10^{-3}]$

ΔH of the reaction comes out to be negative. Hence, reaction is exothermic.

7. (a, b, c, d)

8. (d) :
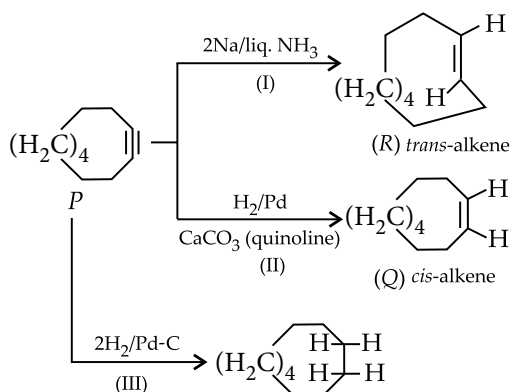
9. (b, c) : The reaction mechanism is :
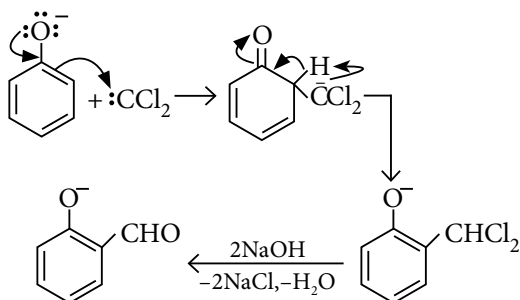
10. (a, b, c) : $P = 110x_A + 125x_B$

$n_A = n_B$

$\therefore \quad x_A = x_B = \dfrac{1}{2}$

$P = 110 \times \dfrac{1}{2} + 125 \times \dfrac{1}{2} = 117.5$ mm Hg

When B is pure $x_B = 1$ and $x_A = 0$

$p_B^\circ = 125$ mm Hg

Hence, $P < p_B^\circ$,

When A is pure $x_A = 1$ and $x_B = 0$

$p_A^\circ = 110$

Hence, $P > p_A^\circ$.

11. (a, b, c)

12. (a,b,d) :

Nickel dimethylglyoximate (II)
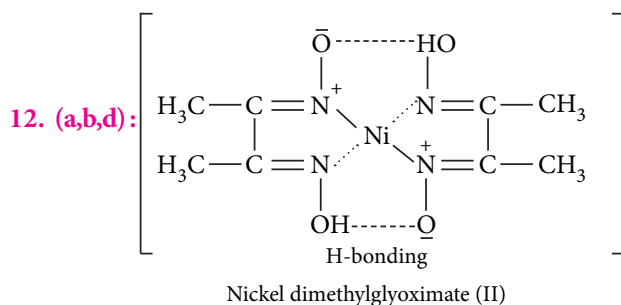
13. (a) : It is the Hunsdiecker reaction.

14. (b, d) : Due to delocalisation of electrons of the N-atom over the benzene ring in aniline (III) and involvement of these electrons in aromatic sextet formation in pyrrole (I), both these amines are weaker bases than pyridine (II). In pyridine (II) such a delocalisation does not exist as the lone pair of electrons is present in a sp^2-hybridised orbital which lies outside the plane of the ring. Hence, II is more basic than I and III. Further, I is weak acid with $pK_a = 17.5$.

15. (c)　　　　　　　　**16. (d)**

17. (c) :

18. (b) :

◈ ◈

PRACTICE PAPER
BITSAT

Exam date: 16th to 30th May 2017

1. Which of the following statements is correct?
   (a) Elements of group 15 form electron deficient hydrides.
   (b) All elements of group 14 form electron precise hydrides.
   (c) Electron precise hydrides have octahedral geometries.
   (d) Electron rich hydrides can act as Lewis acids.

2. The blue colour of copper sulphate disappears on adding zinc granules to it. This is due to
   (a) oxidation of Zn^{2+} ions
   (b) reduction of Cu^{2+} ions
   (c) oxidation of Cu atoms
   (d) reduction of Zn^{2+} ions.

3. Consider the following reactions,
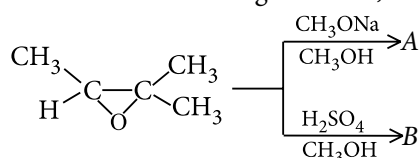
   and choose the correct answer.
   (a) A and B both are 3-methoxy-3-methyl-2-butanol.
   (b) A and B both are 3-methoxy-2-methyl-2-butanol.
   (c) A is 3-methoxy-2-methyl-2-butanol and B is 3-methoxy-3-methyl-2-butanol.
   (d) A is 3-methoxy-3-methyl-2-butanol and B is 3-methoxy-2-methyl-2-butanol.

4. The nucleus of an atom can be assumed to be spherical. The radius of the nucleus of mass number A is given by $1.25 \times 10^{-13} \times A^{1/3}$ cm. Radius of atom is 1 Å. If the mass number is 64, then the fraction of the atomic volume that is occupied by the nucleus is
   (a) 1.0×10^{-3} (b) 5.0×10^{-5}
   (c) 2.5×10^{-2} (d) 1.25×10^{-13}

5. When electronic transition occurs from higher energy state to a lower energy state, with energy difference equal to ΔE eV, the wavelength of line emitted is approximately equal to
   (a) $\dfrac{12400}{\Delta E} \times 10^{-10}$ m   (b) $\dfrac{13397}{\Delta E} \times 10^{10}$ m
   (c) $\dfrac{14322}{\Delta E} \times 10^{-10}$ cm   (d) $\dfrac{12387}{\Delta E} \times 10^{10}$ cm

6. The dispersed phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged respectively. Which of the following statements is not correct?
   (a) Magnesium chloride solution coagulates gold sol readily than iron (III) hydroxide sol.
   (b) Sodium sulphate solution causes coagulation in both sols.
   (c) Mixing of the two sols has no effect.
   (d) Coagulation in both sols can be brought about by electrophoresis.

7. Match the CFSE (Crystal Field Stabilisation Energy) given in List-I with electronic configurations in octahedral field given in List-II and select the correct answer using the code given below the lists :

List-I	List-II
(P) $-0.8\,\Delta_o$	(1) t_{2g}^3, e_g^2
(Q) zero	(2) t_{2g}^5, e_g^0
(R) $-1.2\,\Delta_o$	(3) t_{2g}^2, e_g^0
(S) $-2.0\,\Delta_o$	(4) t_{2g}^3, e_g^0

	P	Q	R	S
(a)	3	1	4	2
(b)	4	3	1	2
(c)	3	2	4	1
(d)	2	1	4	3

8. Which of the following is arranged in order of increasing bond strength?
   (a) $Zn_2^{2+} < Hg_2^{2+} < Cd_2^{2+}$
   (b) $Cd_2^{2+} < Hg_2^{2+} < Zn_2^{2+}$
   (c) $Zn_2^{2+} < Cd_2^{2+} < Hg_2^{2+}$
   (d) $Hg_2^{2+} < Cd_2^{2+} < Zn_2^{2+}$

9. $Cr_2O_7^{2-} + X \xrightarrow{H^+} Cr^{3+} + H_2O + \text{oxidised product of } X$
   X in the above reaction cannot be
   (a) $C_2O_4^{2-}$ (b) SO_4^{2-}
   (c) S^{2-} (d) Fe^{2+}

10. Which of the following will show optical activity?
    (a) [structure: $H_2C=C(H)-C(H)=C(CH_3)-CH(Cl)CH_3$]
    (b) [structure with CH_3, H, $C=C$, $CH(CH_3)_2$]
    (c) [structure with CH_3, H, $C=C$, CH_3, $CHCl_2$]
    (d) None of these
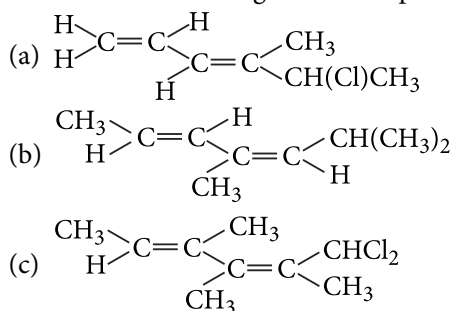
11. Which one of the following statements is correct regarding carbenes?
    (a) These are reactive, short-lived, diagonal in geometry and neutral species in which carbon atom has six electrons in the outer shell.
    (b) They are divalent carbon species containing two unpaired electrons and possess no charge.
    (c) These are of two types, (I) singlet carbene where both the electrons go into one orbital and have opposite spins, (II) triplet carbene where the two electrons go into different orbitals and have same spin (parallel) hence, shows paramagnetic moment. They would exist in three closely grouped energy state if placed in magnetic field.
    (d) All of these.

12. The energy difference between (d_{xy}, d_{yz}, d_{zx}) orbitals and $(d_{x^2-y^2}, d_{z^2})$ orbitals in tetrahedral complex is considerably less than that in octahedral field. One of the reasons is that,
    (a) there are only four ligands in tetrahedral complex instead of six in octahedral complex
    (b) the direction of the orbital lobes coincides with the direction of the ligands

(c) there is high steric repulsion between four ligands approaching tetrahedrally towards metal ion
(d) all the lobes of d-orbitals point towards the ligands in octahedral but in tetrahedral only half of the lobes of d-orbitals point towards the ligand.

13. Using the following information, choose the correct order of activity of the metals as reducing agents :
    (i) Cr reacts with $NiBr_2$ and $CdBr_2$, but not with $ZnBr_2$.
    (ii) Cd reacts with $NiBr_2$, but not with $ZnBr_2$ and $CrBr_3$.
    (a) Zn > Cr > Cd > Ni   (b) Ni > Cr > Cd > Zn
    (c) Zn > Cr > Ni > Cd   (d) Zn > Cd > Cr > Ni

14. Which of the following diagrams is correct in relation to electron affinity of halogens?

    (a) F →(decrease) Cl; F ↑(increase) I; I ←(decrease) Br; Cl ↓(decrease) Br
    (b) F →(decrease) Cl; F ↑(decrease) I; I ←(decrease) Br; Cl ↓(decrease) Br
    (c) F →(increase) Cl; F ↑(increase) I; I ←(decrease) Br; Cl ↓(decrease) Br
    (d) F →(increase) Cl; F ↑(decrease) I; I ←(decrease) Br; Cl ↓(increase) Br
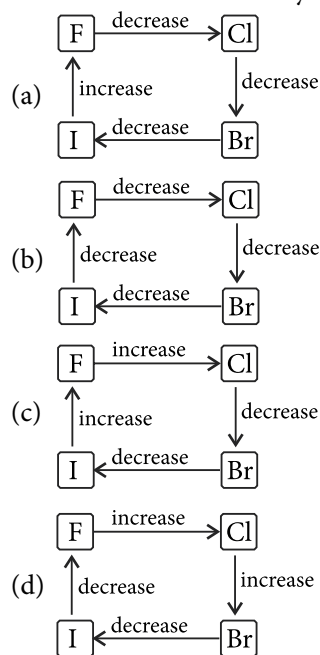
15. What is the order of spin only magnetic moment of the following systems?
    I. Mn^{2+} in presence of weak field ligand in octahedral field.
    II. Ni^{2+} in presence of strong field ligand in octahedral field.
    III. Cr^{3+} in presence of CN^- ligand in octahedral field.
    IV. Sc^{3+} in presence of weak field ligand in octahedral field.
    (a) II > III > IV > I   (b) I > III > II > IV
    (c) III > IV > II > I   (d) I > IV > III > II

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16. Which of the following properties shows given change in NH_4^+, NH_3 and NH_2^-?

$$\boxed{NH_4^+} \xrightarrow{\text{Decrease}} \boxed{NH_3}$$

Increase — Decrease

$$\boxed{NH_2^-}$$
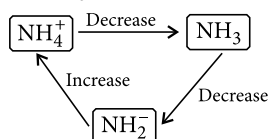
(a) Number of lone pairs at nitrogen
(b) Total number of electrons
(c) Number of p-orbitals in hybridisation of nitrogen
(d) Bond angle at nitrogen

17. A cylinder of compressed gas that bears no label is supposed to contain ethylene and/or propylene. Combustion of the sample shows that 16 mL of the gas required 72 mL of oxygen for complete combustion. This indicates that the gas is
(a) only ethylene
(b) only propylene
(c) 1 : 1 mixture of two gases
(d) some unknown mixture of two gases.

18. Hydrolysis product of which of the following compounds produces white precipitate with Tollens' reagent?
(a) SiC
(b) Be_2C
(c) Mg_2C_3
(d) Al_4C_3

19. The incorrect statement amongst the following is
(a) $LiAlH_4$ and $NaBH_4$ act as reducing agents due to the presence of hydride ion
(b) Al—H bond is more ionic than B—H bond and hence, $LiAlH_4$ can produce larger concentration of hydride ions than $NaBH_4$
(c) $LiAlH_4$ cannot reduce —NO_2 group
(d) inspite of very small rate constant of reduction of any carbonyl function other than aldehydes and ketones, the rate of reduction with $LiAlH_4$ becomes appreciable due to large concentration of hydride ions.

20. A compound is analysed and found to consist of 50.4% Ce, 15.1% N and 34.5% O by mass. What is the correct empirical formula of the compound? (At. wt. of Ce = 140)
(a) $Ce_2(NO_3)_2$
(b) $Ce_2(NO_2)_3$
(c) $Ce(NO_3)_2$
(d) $Ce(NO_2)_3$

21. n_1 and n_2 moles of two ideal gases having molecular weights M_1 and M_2 respectively at temperatures T_1 K and T_2 K are mixed. Assuming no loss of energy, the temperature of mixture will become
(a) $n_1 T_1 + n_2 T_2$
(b) $\dfrac{n_1 T_1 + n_2 T_2}{T_1 + T_2}$
(c) $\dfrac{n_1 T_1 + n_2 T_2}{n_1 + n_2}$
(d) $\dfrac{T_1 \times T_2}{n_1 \times n_2}$

22. Which of the following reactions is incorrectly represented?

(a) [structure: F-substituted nitrobenzene $\xrightarrow{NaOCH_3}$ OCH$_3$-substituted nitrobenzene]

(b) [structure with C_6H_5, O, Br $\xrightarrow{NaOH\ (aq.)}$ benzofuran with C_6H_5]

(c) [structure with CH$_3$, CH, CH$_3$, Br $\xrightarrow{NaOH\ (aq.)}$ product with CH$_3$, CH, CH$_3$, HO]

(d) [structure with F, O_2N, CH_3 $\xrightarrow{NaOH\ (aq.)}$ product with OH, O_2N, CH_3]
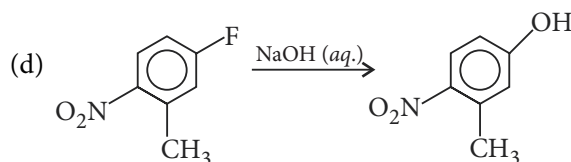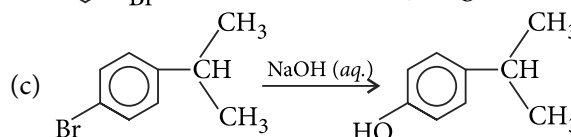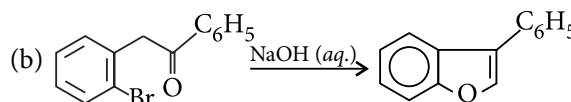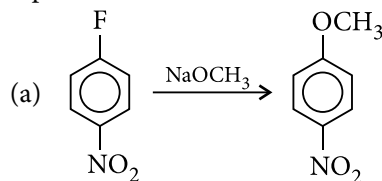
23. In a compound, [benzene ring]—E electrophilic substitution has occured. The substituent E can be –CH_3, –CH_2Cl, –CCl_3 and –$CHCl_2$. The correct increasing order towards electrophilic substitution is
(a) $- CH_3 < - CH_2Cl < - CHCl_2 < - CCl_3$
(b) $- CH_3 < - CHCl_2 < - CH_2Cl < - CCl_3$
(c) $- CCl_3 < - CH_2Cl < - CHCl_2 < - CH_3$
(d) $- CCl_3 < - CHCl_2 < - CH_2Cl < - CH_3$

24. The hydrolysis constant for the reaction,
$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$
is 1.4×10^{-12}. The ionisation constant for
$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$ will be
(a) 7.14×10^{-3}
(b) 1.4×10^{-12}
(c) 7.14×10^{-12}
(d) 1.4×10^{-3}

25. The rate of reaction, $2NO + Cl_2 \rightarrow 2NOCl$, is given by the rate equation, rate = $k\,[NO]^2[Cl_2]$. The value of the rate constant can be increased by
(a) increasing the temperature
(b) increasing the concentration of NO
(c) increasing the concentration of Cl_2
(d) all of these.

26. The combustion of 10.0 g coke raised the temperature of 1.0 kg water from 10°C to 50°C. If specific heat of H_2O is 1 cal/(g°C) then, the fuel value of coke is
(a) 1000 cal/g
(b) 2000 cal/g
(c) 3000 cal/g
(d) 4000 cal/g

27. If 3 faradays of electricity is passed through each of the solutions of $AgNO_3$, $CuSO_4$ and $AuCl_3$, the molar ratio of the cations deposited at the cathode will be
(a) $1:1:1$ (b) $1:2:3$
(c) $3:2:1$ (d) $6:3:2$

28. A crystalline solid has a cubic structure in which tungsten (W) atoms are located at the cube corners of the unit cell, oxygen atoms at the cube edges and sodium atoms at the cube centre. The molecular formula of the compound is
(a) Na_2WO_3 (b) $NaWO_4$
(c) $NaWO_3$ (d) Na_2WO_4

29. Which of the following colligative properties can provide molar mass of proteins (or polymers or colloids) with greater precision?
(a) Relative lowering of vapour pressure
(b) Elevation in boiling point
(c) Depression in freezing point
(d) Osmotic pressure

30. Compound (*A*) reacts with $SOCl_2$ to give compound (*B*). The compound (*B*) reacts with Mg metal to give Grignard reagent, which is treated with acetone and product is hydrolysed to give 2-methyl -2-butanol. Which of the following is compound (*A*)?
(a) CH_3CH_2OH (b) $CH_3CH_2CH_2OH$
(c) CH_3OH (d) CH_3COOH

31. Consider the following compounds with regard to their reactivities towards nucleophilic acyl substitution by a given nucleophile.

$$CH_3-\underset{I}{\overset{O}{\overset{||}{C}}}OCH_3 \qquad CH_3-\underset{II}{\overset{O}{\overset{||}{C}}}OCH_2CCl_3$$

$$CH_3-\underset{III}{\overset{O}{\overset{||}{C}}}OCH_2CF_3$$

The order of decreasing reactivity is
(a) I > II > III   (b) III > II > I
(c) II > III > I   (d) I > III > II

32. What is the end product (*B*) in the following reaction sequence?

$$C_6H_5-\overset{H}{\underset{}{C}}=O + CH_3NO_2 \xrightarrow{KOH/C_2H_5OH} A \xrightarrow[\Delta]{-H_2O} B$$

(a) $C_6H_5NH_2$
(b) $C_6H_5CH=CH-NO_2$
(c) $C_6H_5CHOHCH_3$ (d) $C_6H_5NO_2$

33. Match the column I with column II, and select the correct option.

	Column I		Column II
1.	Acidic amino acid	(A)	Glycine
2.	Sulphur containing amino acid	(B)	Histidine
3.	Essential amino acid	(C)	Cysteine
4.	Optically inactive amino acid	(D)	Glutamic acid

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

34. An organic compound '*A*' burns with a sooty flame. It gives negative test towards Tollens' reagent and positive test for Brady's reagent. The compound '*A*' is
(a) acetophenone   (b) acetone
(c) salicylic acid   (d) benzaldehyde.

35. For the given sequence of reactions,

the major product is

36. Half life of a radioactive sample is $2x$ years. What fraction of this sample will remain undecayed after x years?
(a) $\dfrac{1}{2}$ (b) $\dfrac{1}{\sqrt{2}}$ (c) $\dfrac{1}{\sqrt{3}}$ (d) 2

37. In the following reaction,

$$Ethene \xrightarrow[350-570 \text{ K, traces of } O_2]{1000-2000 \text{ atm}} A$$

A is
(a) HDPE   (b) LDPE
(c) teflon   (d) melamine.

38. When sulphur in the form of S_8 is heated at 900 K, the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 into S_2. The value of equilibrium constant for this reaction is

(a) 2.55   (b) 9.9×10^{-3}
(c) 11×10^{-2} (d) 1.89

39. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is
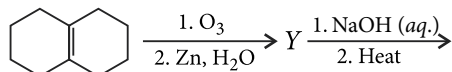
(a) one   (b) two
(c) three   (d) four.

40. Match the column I with column II and choose the correct option.

Column I		Column II
1.	Antacid	(p) Naproxen
2.	Antihistamine	(q) Prontosil
3.	Analgesic	(r) Terfenadine
4.	Antibacterial drug	(s) Ranitidine

(a) 1-(s), 2-(r), 3-(p), 4-(q)
(b) 1-(q), 2-(p), 3-(r), 4-(s)
(c) 1-(p), 2-(q), 3-(s), 4-(r)
(d) 1-(r), 2-(s), 3-(q), 4-(p)

SOLUTIONS

1. (b): Elements of group 14 form electron precise hydrides which have tetrahedral geometry.

2. (b):
$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$
or $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
or $Cu^{2+} + 2e^- \rightarrow Cu$

Since, Cu^{2+} accepts electrons, it gets reduced.

3. (c): In presence of acids, nucleophile attacks the more substituted carbon of the epoxide while in presence of bases, the nucleophilic attack occurs at the less crowded carbon, *i.e.*,

3-Methoxy-2-methyl-2-butanol
(A)

(more stable carbocation)

3-Methoxy-3-methyl-2-butanol
(B)
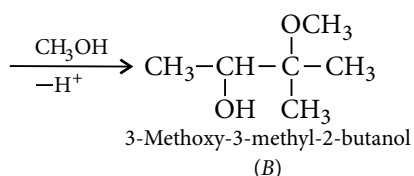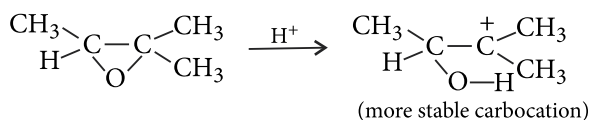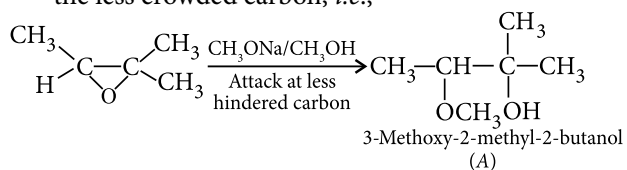
4. (d): Radius of nucleus $= 1.25 \times 10^{-13} \times A^{1/3}$ cm
$= 1.25 \times 10^{-13} \times 64^{1/3}$ cm
$= 1.25 \times 10^{-13} \times 4$ cm $= 5 \times 10^{-13}$ cm
Radius of atom $= 1$ Å $= 10^{-8}$ cm
Volume of nucleus/volume of atom
$$= \frac{(4/3)\pi(5\times10^{-13})^3}{(4/3)\pi(10^{-8})^3} = \frac{125\times10^{-39}}{10^{-24}}$$
$= 125 \times 10^{-15} = 1.25 \times 10^{-13}$

5. (a): $\lambda = \dfrac{hc}{\Delta E} = \dfrac{6.626\times10^{-34}\times3\times10^8}{\Delta E \times 1.602\times10^{-19}}$ m
$$= \frac{12.40\times10^{-7}}{\Delta E}\text{ m} \quad \text{or} \quad \frac{12400\times10^{-10}}{\Delta E}\text{ m}$$

6. (c): Mixing of +ve and –ve sols causes mutual coagulation.

7. (a): For a metal having $t_{2g}^x e_g^y$ configuration,
CFSE $= (-0.4x + 0.6y)\,\Delta_o$
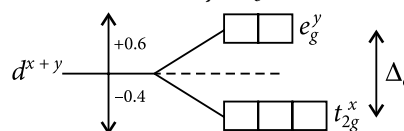
8. (c): Due to poor shielding of $4f$ electrons, bond strength is maximum for Hg^+—Hg^+.

9. (b): $Cr_2O_7^{2-} + X \xrightarrow{H^+} Cr^{3+} + H_2O$
$\qquad\qquad\qquad + $ oxidised product of X
In the given reaction, X is oxidised and hence, acting as a reducing agent. Out of the given choices, SO_4^{2-} cannot act as a reducing agent, because sulphur is present in its highest oxidation state, *i.e.*, +6.

10. (a):

11. (d)   **12. (a)**   **13. (a)**

14. (c): Electron affinity of halogens follows the order:
Cl > F > Br > I.

15. (b): (I) Mn^{2+} : $[Ar]3d^5 4s^0$
In presence of weak field ligand in octahedral field;
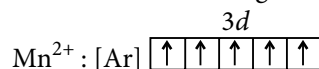
$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35}$ B.M.

(II) Ni^{2+} : $[Ar]3d^8 4s^0$
In presence of strong field ligand in octahedral field ;

Ni^{2+} : [Ar] $\boxed{\uparrow\downarrow|\uparrow\downarrow|\uparrow\downarrow|\uparrow|\uparrow}$ $3d$

$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8}$ B.M.

(III) Cr^{3+} : $[Ar]3d^3 4s^0$

In presence of CN^- ligand in octahedral field ;

Cr^{3+} : [Ar] $\boxed{\uparrow|\uparrow|\uparrow| \ |}$ $3d$

$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$ B.M.

(IV) Sc^{3+} : $[Ar]3d^0 4s^0$
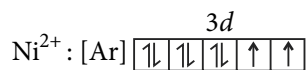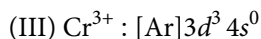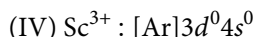
$n = 0, \ \mu = 0$

16. (d): Bond angle follows the order :
$NH_4^+ > NH_3 > NH_2^-$
(109.5°) (107°) (105°)
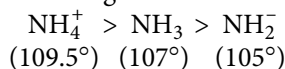
17. (b) : $CH_2{=}CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

22,400 mL of ethylene requires $3 \times 22,400$ mL of O_2 for complete combustion.

$\therefore$ 16 mL of ethylene will require

$= 3 \times 22,400 \times \dfrac{1}{22,400} \times 16 = 48$ mL of O_2

$CH_3{-}CH{=}CH_2 + \dfrac{9}{2} O_2 \longrightarrow 3CO_2 + 3H_2O$
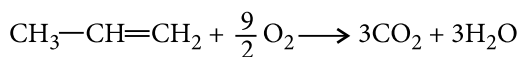
22,400 mL of propylene requires $\dfrac{9}{2} \times 22,400$ mL of O_2 for complete combustion.

$\therefore$ 16 mL of propylene will require

$= \dfrac{9}{2} \times 22,400 \times \dfrac{1}{22,400} \times 16 = 72$ mL of O_2

Therefore, the gas is propylene.

18. (c) :
$Mg_2C_3 + 4H_2O \rightarrow 2Mg(OH)_2 + H_3C{-}C{\equiv}CH$
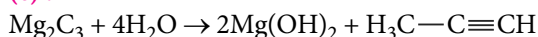
Terminal alkyne produces white precipitate with Tollens' reagent.

19. (c) : $LiAlH_4$ can reduce $-NO_2$ group to $-NH_2$ group.

20. (d):

	Ce	N	O
Percentage:	50.4	15.1	34.5
Moles:	$\dfrac{50.4}{140}=0.36$	$\dfrac{15.1}{14}=1.07$	$\dfrac{34.6}{16}=2.15$
Simplest ratio:	1	3	6

Thus, the formula is $Ce(NO_2)_3$.

21. (c) : Let the final temperature be T, then

$KE_1 + KE_2 = KE_{mixture}$

$\dfrac{3}{2}n_1RT_1 + \dfrac{3}{2}n_2RT_2 = \dfrac{3}{2}(n_1+n_2)RT$

$\therefore \quad T = \dfrac{n_1T_1 + n_2T_2}{n_1 + n_2}$

22. (c)

23. (d): Chlorine atoms are electro negative (show $-I$ effect). They deactivate the ring towards electrophilic substitution reactions.

24. (a) : $K_h = \dfrac{[H_3PO_4][OH^-]}{[H_2PO_4^-]}$

and $K_a = \dfrac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]}$

$\therefore \quad K_h = \dfrac{[H_3O^+][OH^-]}{K_a} = \dfrac{K_w}{K_a}$

$\therefore \quad K_a = \dfrac{K_w}{K_h} = \dfrac{10^{-14}}{1.4\times10^{-12}} = 7.14\times10^{-3}$

25. (a): The rate constant of a reaction depends only on temperature and does not depend upon concentrations of the reactants.

26. (d): Heat supplied to heat water $= ms\Delta T$
$= 10^3 \times 1 \times 40 = 40 \times 10^3$ cal

Calorific value $= \dfrac{\Delta H}{\text{Weight of fuel}} = \dfrac{40\times10^3}{10}$
$= 4000$ cal g^{-1}

27. (d): $AgNO_3$: $\underset{1F}{Ag^+} + e^- \rightarrow \underset{1\,mol}{Ag}$
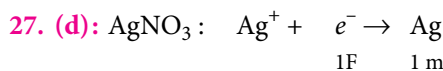
$\therefore$ 3 faradays of electricity will deposit 3 moles of Ag.

$CuSO_4$: $\underset{2F}{Cu^{2+}} + 2e^- \rightarrow \underset{1\,mol}{Cu}$
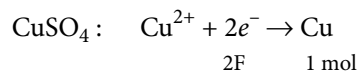
$\therefore$ 3 faradays of electricity will deposit $\dfrac{3}{2}$ moles of Cu.

$AuCl_3$: $\underset{3F}{Au^{3+}} + 3e^- \rightarrow \underset{1\,mol}{Au}$
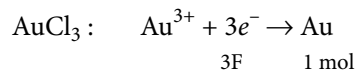
$\therefore$ 3 faradays of electricity will deposit 1 mole of Au.
Thus, Ag : Cu : Au $= 3 : 3/2 : 1$, *i.e.*, $6 : 3 : 2$.

28. (c) : Number of W-atoms (present at cube corners) per unit cell $= \dfrac{1}{8} \times 8 = 1$

Number of O-atoms (present at cube edges) per unit cell $= \dfrac{1}{4} \times 12 = 3$

Number of Na-atoms (present at cube centre) per unit cell $= 1$

Thus, Na : W : O $= 1 : 1 : 3$
Thus, formula of the compound is $NaWO_3$.

29. (d): Molar mass of macromolecules (proteins, polymers or colloids, etc.) can be determined with greater precision by finding osmotic pressure because the magnitude of this colligative property is comparatively large even in dilute solutions.

30. (a): $CH_3CH_2OH \xrightarrow{SOCl_2} CH_3CH_2Cl \xrightarrow{Mg}$
$\qquad\qquad (A) \qquad\qquad\qquad (B)$

$\qquad\qquad\qquad\qquad CH_3CH_2MgCl$

$CH_3CH_2MgCl + CH_3COCH_3 \xrightarrow[H_3O^+]{dry\ ether}$

$\qquad\qquad CH_3C(CH_3)(OH)CH_2CH_3$
$\qquad\qquad\qquad 2\text{-Methyl-2-butanol}$
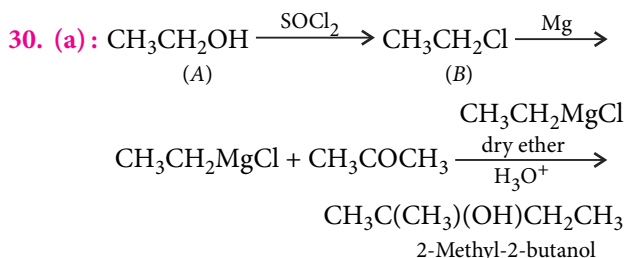
31. (b): Higher the electron deficiency on carbonyl carbon atom, greater is the reactivity towards acyl substitution.

32. (b):

$$C_6H_5\overset{\displaystyle H}{-\underset{\ }{C}}=O + CH_3NO_2 \xrightarrow{KOH/C_2H_5OH}$$

$$C_6H_5-CH=CH-NO_2 \xleftarrow[\Delta]{-H_2O} C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_2NO_2$$
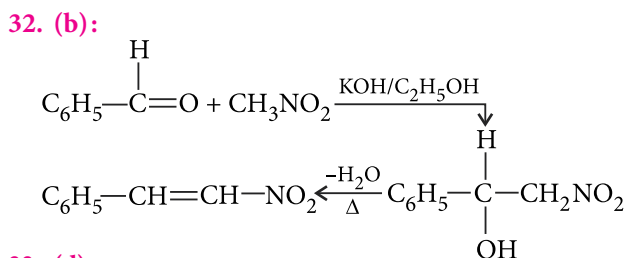
33. (d)

34. (a): Since, given compound 'A' burns with a sooty flame therefore, it must be an aromatic compound. Again, when it reacts with Brady's reagent (acidic 2, 4-dinitrophenylhydrazine solution), it yields an orange precipitate. Therefore, it must be an aldehyde or ketone. But ketone does not give Tollens' reagent test therefore, it must be a ketone. Hence, 'A' is acetophenone.

35. (c):
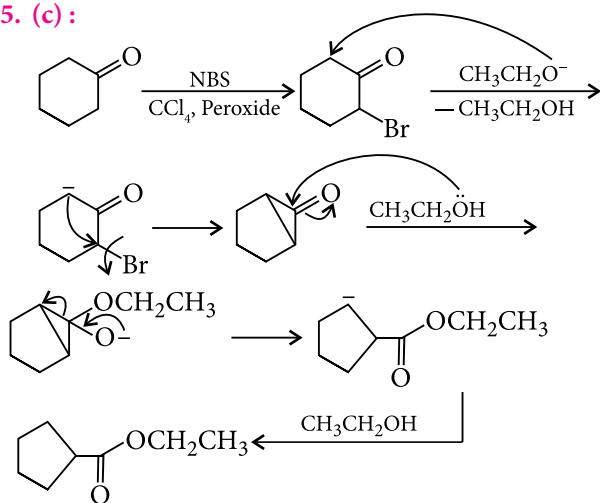
This is Favorskii rearrangement.

36. (b): $\lambda = \dfrac{2.303}{t}\log_{10}\left(\dfrac{N_0}{N}\right)$ and $\lambda = \dfrac{0.693}{t_{1/2}}$

$$\dfrac{0.693}{t_{1/2}} = \dfrac{2.303}{t}\log_{10}\left(\dfrac{N_0}{N}\right)$$

$$\dfrac{0.693}{2x} = \dfrac{2.303}{x}\log_{10}\left(\dfrac{N_0}{N}\right)$$

$$0.15 = \log_{10}\left(\dfrac{N_0}{N}\right)$$

Taking antilog;

$$\dfrac{N_0}{N} = \sqrt{2} \Rightarrow \dfrac{N}{N_0} = \dfrac{1}{\sqrt{2}}$$

$\therefore$ Fraction undecayed $= \dfrac{1}{\sqrt{2}}$

37. (b): Ethene $\xrightarrow[350-570\ K,\ traces\ of\ O_2]{1000-2000\ atm}$ LDPE

38. (a):

	$S_{8(g)}$	$\rightleftharpoons$	$4S_{2(g)}$
Initially :	1 atm		0
At equilibrium :	$1-\dfrac{29}{100}$		0.29×4
	= 0.71 atm		= 1.16 atm
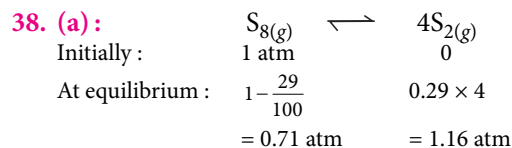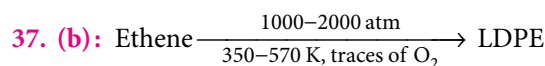
Equilibrium constant $(K_p) = \dfrac{[p_{S_2}]^4}{[p_{S_8}]} = \dfrac{[1.16]^4}{0.71} = 2.55$

39. (a):
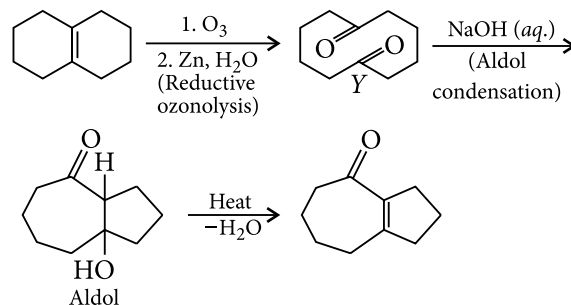
Since, diketone (Y) is symmetrical, therefore, upon intramolecular aldol condensation, it gives only one product.

40. (a)

··· ◈◈

MPP-1 CLASS XI		ANSWER	KEY	
1. (c)	**2.** (a)	**3.** (b)	**4.** (c)	**5.** (d)
6. (b)	**7.** (d)	**8.** (a)	**9.** (b)	**10.** (c)
11. (d)	**12.** (a)	**13.** (b)	**14.** (b)	**15.** (c)
16. (a)	**17.** (c)	**18.** (d)	**19.** (d)	**20.** (b,d)
21. (b,c,d)	**22.** (b,c)	**23.** (a,c)	**24.** (6)	**25.** (6)
26. (3)	**27.** (d)	**28.** (d)	**29.** (b)	**30.** (d)
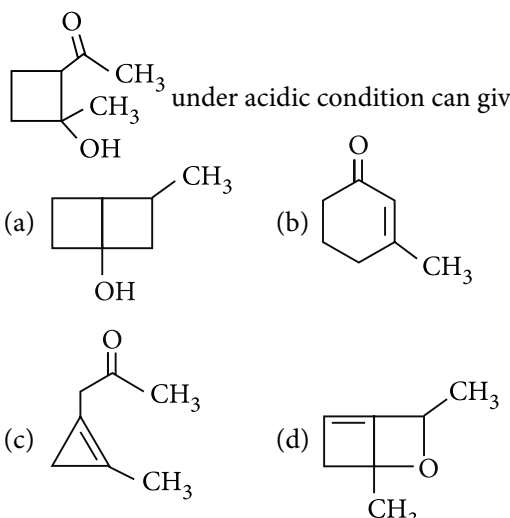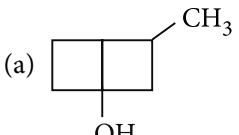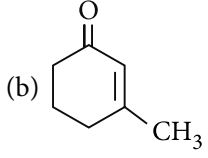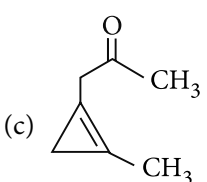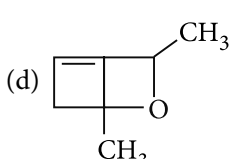
PRACTICE PAPER
AIIMS

Exam on 28th May

1. The behaviour of a real gas is usually depicted by plotting compressibility factor Z vs P at a constant temperature. At high temperature and high pressure, Z is usually more than one. This fact can be explained by van der Waals' equation when
   (a) the constant a is negligible
   (b) the constant b is negligible
   (c) both the constants a and b are not negligible
   (d) both the constants a and b are negligible.

2. The standard heat of combustion of Al is $-837.8 \text{ kJ mol}^{-1}$ at 25°C. If Al reacts with O_2 at 25°C, which of the following releases 250 kJ of heat?
   (a) The reaction of 0.624 mol of Al.
   (b) The formation of 0.624 mol of Al_2O_3.
   (c) The reaction of 0.312 mol of Al.
   (d) The formation of 0.150 mol of Al_2O_3.

3. 100 mL of 0.1 N hypo solution decolourises iodine by the addition of x g of crystalline copper sulphate to excess of KI. The value of 'x' is
   (Molar mass of $CuSO_4 \cdot 5H_2O$ = 250 g/mol).
   (a) 5 g   (b) 1.25 g   (c) 2.5 g   (d) 4 g

4. You want to prepare 3-methyloctane by Corey-House synthesis. Which of the following pairs would be the worst to start with?
   (a) $[H_3CCH_2CH_2CH_2CH_2]_2CuLi$ and

   $H_3CCH_2 - \overset{\underset{|}{CH_3}}{CH} - Br$

   (b) $[H_3CCH_2 - \overset{\underset{|}{CH_3}}{CH}]_2CuLi$ and

   $H_3CCH_2CH_2CH_2CH_2Br$

   (c) $[H_3CCH_2CH_2CH_2CH_2\overset{\underset{|}{CH_3}}{CH}]_2CuLi$ and

   CH_3CH_2Br

   (d) $[H_3CCH_2CH_2CH_2CH_2\overset{\underset{|}{CH_3}}{CHCH_2}]_2CuLi$

   and CH_3Br

5. The final products B and C formed in the following sequence of reactions,

   are respectively
   (a) both bromobenzene
   (b) o-bromonitrobenzene and p-bromonitrobenzene
   (c) m-bromonitrobenzene and p-bromonitrobenzene
   (d) p-bromonitrobenzene and o-bromonitrobenzene.

6. For the reaction $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, the values of K_p are 1.7×10^3 at 500 K and 1.7×10^4 at 600 K. Which of the following is correct?
   (a) The proportion of NO_2 in the equilibrium mixture is increased by decrease in pressure.
   (b) The standard enthalpy change for the forward reaction is negative.
   (c) Unit of K_p is atm^{-1}.
   (d) At 500 K, the degree of dissociation of N_2O_4 decreases by 50% by increasing the pressure by 100%.

7. Half litre of each of three samples of 10 volume, 15 volume and 20 volume H_2O_2 are mixed and equal volume of water is added. The volume strength of the resulting solution is
   (a) 1.04   (b) 2.08   (c) 6.5   (d) 7.5

8. Alkali metal ion complexes are characterised with chelating organic reagents such as salicylaldehyde and polyethers. Which of the following is the correct order of equilibrium formation for above complexes?

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

9. The reaction, $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$ ($\Delta G° = -421$ kJ) is thermodynamically feasible due to negative value of $\Delta G°$. Why does this reaction not take place at room temperature?
   (a) Certain amount of activation energy is essential for thermodynamically feasible reactions also.
   (b) Due to high melting point of chromium oxide the reaction does not take place.
   (c) Overall value of ΔG for the net reaction becomes positive.
   (d) Molecules of Cr_2O_3 and Al are not oriented properly.

10. The element with the outer electronic configuration, $3d^5 4s^2$ will be expected to
    I.   form coloured ions
    II. form complex compounds
    III. have a low melting point.
    Choose the correct statement(s).
    (a) Only I   (b) Only I and II
    (c) Only III   (d) All of these

11. Which of the following arrangements is correct on the basis of increasing p-character of hybrid orbitals of the central atom?
    (a) $ZnCl_2 < SnCl_2 < SO_4^{2-}$
    (b) $SnCl_2 < ZnCl_2 < SO_4^{2-}$
    (c) $ZnCl_2 < SO_4^{2-} < SnCl_2$
    (d) $SO_4^{2-} < ZnCl_2 < SnCl_2$

12. under acidic condition can give

(a)   (b)

(c)   (d)

13. For an ideal binary liquid solution with $P_A° > P_B°$ which relation between X_A (mole fraction of A in liquid phase) and Y_A (mole fraction of A in vapour phase) is correct? [Assuming X_B and Y_B are mole fractions of B in liquid and vapour phase respectively.]
    (a) $X_A = Y_A$ (b) $X_A > Y_A$
    (c) $\dfrac{X_A}{X_B} > \dfrac{Y_A}{Y_B}$
    (d) X_A, Y_A, X_B and Y_B cannot be correlated.

14. A drop of solution (volume 0.05 mL) contains 3.0×10^{-6} mole of H^+. If the rate constant of disappearance of H^+ is 1.0×10^7 mol L^{-1} sec^{-1}. How long would it take for H^+ in that drop to disappear?
    (a) 6×10^{-8} sec   (b) 6×10^{-7} sec
    (c) 6×10^{-9} sec   (d) 6×10^{-10} sec

15. Out of the given statements, select the incorrect one.
    (a) $NaClO_4$ is water soluble but $KClO_4$ is not.
    (b) $Na_3[Co(NO_2)_6]$ is water soluble but $K_3[Co(NO_2)_6]$ is not.
    (c) Na_2CO_3 is water soluble but $CaCO_3$ is not.
    (d) NaCl is water soluble but $CaCl_2$ is not.

16. The increasing order of boiling points of the following compounds is
    (I) catechol   (II) resorcinol
    (III) hydroquinone   (IV) phenol
    (a) I < II < IV < III   (b) I < II < III < IV
    (c) IV < II < I < III   (d) IV < I < II < III

17. Which of the following is not correct about the given reaction?
    $$CH_2 = CH_2 + Br_2 \xrightarrow{\text{NaI}(aq.)}$$
    (a) The products formed are CH_2BrCH_2Br and CH_2BrCH_2I.
    (b) The reaction follows polar mechanism.
    (c) The reaction occurs readily in solution and is catalysed by inorganic halides.
    (d) Only CH_2ICH_2I is formed.

18. A beaker containing 20 g sugar in 100 g water and another containing 10 g sugar in 100 g water are placed under a bell-jar and allowed to stand until equilibrium is reached. The amount of water which will be transferred from one beaker to other is
    (a) 11.0 g   (b) 20 g
    (c) 33.3 g   (d) 066.7 g

19. A solid element (symbol Y) conducts electricity and forms two chlorides YCl_n (a colourless volatile liquid) and YCl_{n-2} (a colourless solid). To which one of the following groups of the periodic table does Y belong?
(a) 13   (b) 14   (c) 15   (d) 16

20. Identify the final product of the following reaction.
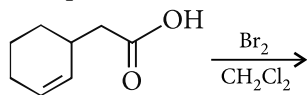
21. The e.m.f. of the following Daniell cell at 298 K is E_1.
Zn|ZnSO$_4$ (0.01 M) || CuSO$_4$ (1.0 M) | Cu
When concentration of ZnSO$_4$ is 1.0 M and that of CuSO$_4$ is 0.01 M, the e.m.f. changed to E_2. What is the relationship between E_1 and E_2 ?
(a) $E_1 > E_2$ (b) $E_1 < E_2$
(c) $E_1 = E_2$ (d) $E_2 = 0 \neq E_1$

22. In a pseudo first order hydrolysis of ester in water, the following results were obtained.

t/s	0	30	60	90
Ester/mol L^{-1}	0.55	0.31	0.17	0.085

What will be the average rate of reaction between the time interval 30 to 60 seconds?
(a) 1.91×10^{-2} mol L^{-1} s^{-1}
(b) 4.67×10^{-3} mol L^{-1} s^{-1}
(c) 1.98×10^{-3} mol L^{-1} s^{-1}
(d) 2.07×10^{-2} mol L^{-1} s^{-1}

23. For $[HgI_3]^-$ ion, geometry and magnetic behaviour are respectively
(a) trigonal bipyramidal and paramagnetic
(b) trigonal pyramidal and diamagnetic
(c) trigonal planar and paramagnetic
(d) trigonal planar and diamagnetic.

24. When metal X is treated with sodium hydroxide, a white precipitate (A) is obtained, which is soluble in excess of NaOH to give soluble complex (B). Compound (A) is soluble in dilute HCl and form compound (C). The compound (A) when heated strongly gives (D), which is used to extract metal. Compound 'D' is
(a) aluminium hydroxide
(b) sodium aluminate
(c) aluminium chloride
(d) alumina.

25. Arrange the following in increasing order of their reactivity towards ring bromination.
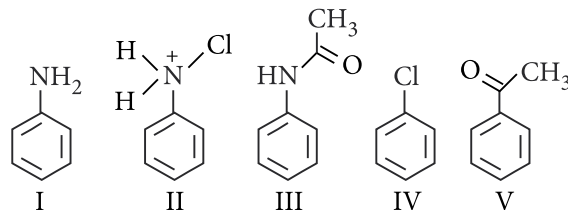
(a) II < V < IV < III < I   (b) II < III < V < IV < I
(c) I < III < V < II < IV   (d) I < IV < V < II < III

26. In the diazotisation of aryl amines with sodium nitrite and hydrochloric acid, an excess of hydrochloric acid is used primarily to
(a) suppress the concentration of free aniline available for coupling
(b) suppress hydrolysis of phenol
(c) ensure a stoichiometric amount of nitrous acid.
(d) neutralise the base liberated.

27. A metal crystallises into two cubic phases, face centred cubic (*fcc*) and body centred cubic (*bcc*), whose unit lengths are 3.5 and 3.0 Å respectively. What will be the ratio of densities of *fcc* to *bcc*?
(a) 1.259 (b) 2.513   (c) 0.892   (d) 1.862

28. A substance which gives a canary yellow precipitate when boiled with an excess of nitric acid and ammonium molybdate and yellow precipitate with AgNO$_3$ is
(a) orthophosphoric acid
(b) pyrophosphoric acid
(c) metaphosphoric acid
(d) hypophosphoric acid.

29. Iodoform gives a precipitate with AgNO$_3$ on heating but chloroform does not because
(a) iodoform is ionic
(b) chloroform is covalent
(c) C — I bond in iodoform is weak and C — Cl bond in chloroform is strong
(d) none of these.

30. Which of the following reactions can give rise to free radicals?

I. Ph—CHO $\xrightarrow{Fe^{3+}}$

II. H_3C—CO—$\overset{-}{CH}$—CO—CH_3 $\xrightarrow{I_2}$

III. Ar—CO—O—O—CO—Ar $\xrightarrow{Cu^+}$
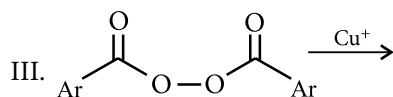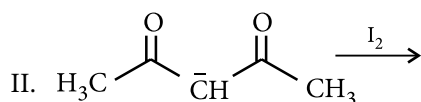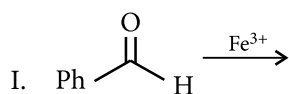
(a) Only I and II   (b) Only II and III
(c) Only I and III   (d) All of these

31. The limiting molar conductivities of HCl, CH_3COONa and NaCl are respectively 425, 90 and 125 mho cm^2 mol^{-1} at 25°C. The molar conductivity of 0.1 M CH_3COOH solution is 7.8 mho cm^2 mol^{-1} at the same temperature. The degree of dissociation of 0.1 M acetic acid solution at the same temperature is
(a) 0.10   (b) 0.02
(c) 0.15   (d) 0.03

32. When a dilute aqueous solution of potassium permanganate is run from a burette into a flask containing dilute aqueous oxalic acid and dilute sulphuric acid, the rate of reaction suddenly increases considerably as more potassium permanganate is added. The best reason for this is that
(a) the manganese (II) ions produced catalyse the reaction
(b) the pH of the solution in flask increases
(c) the reaction is exothermic and the heat liberated increases the rate considerably
(d) the sulphuric acid removes water and so causes the reaction to proceed more rapidly to completion.

33. Select the correct order of number of unpaired electrons in given complexes
(I) A tetrahedral complex with d^6 ion
(II) $[Co(H_2O)_6)]^{2+}$
(III) A complex compound with magnetic moment $\sqrt{35}$ B.M.
(IV) A square planar complex with d^7 ion
(a) III > II > I > IV   (b) I > III > II > IV
(c) III > I > II > IV   (d) IV > II > I > III

34. White phosphorus on reaction with lime water gives calcium salt of an acid (A) along with a gas (X). Which of the following statements is correct?
(a) (A) on heating gives (X) and O_2.
(b) The bond angle in (X) is less than that in case of ammonia.
(c) (A) is a dibasic acid.
(d) (X) is more basic than ammonia.

35. Identify the major products (X, Y and Z) formed in the given reactions.

$C_6H_5OCH_3$ $\xrightarrow[\text{CH}_3\text{Cl, CS}_2]{\text{Anhyd. AlCl}_3,}$ X
$\xrightarrow[\text{CH}_3\text{COCl}]{\text{Anhyd. AlCl}_3,}$ Y
$\xrightarrow[\text{HNO}_3]{\text{H}_2\text{SO}_4}$ Z
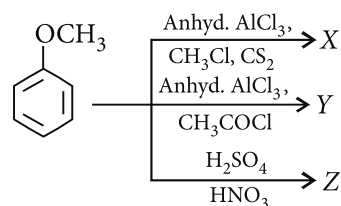
	X	Y	Z
(a)	2-Methoxy-toluene	2-Methoxy-acetophenone	2-Nitroanisole
(b)	4-Nitro-anisole	2-Methoxy-acetophenone	2-Methoxy-toluene
(c)	4-Methoxy-toluene	4-Methoxy-acetophenone	4-Nitroanisole
(d)	4-Methoxy-toluene	2-Methoxy-acetophenone	2-Nitroanisole

36. Although D-galactose rotates plane polarised light but its oxidation product, galactaric acid, does not rotate because,
(a) galactaric acid is a racemic mixture of D-and L-isomer
(b) galactaric acid is a meso compound
(c) both are correct reasons
(d) none is the correct reason.

37. In the following reaction sequence,
$R—CH=CH_2 + H_2SO_4 \longrightarrow$
$(R = C_{16}H_{33})$
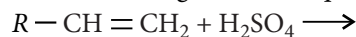
$R—\underset{OSO_3H}{CH}—CH_3$ $\xrightarrow{NaOH}$ $R—\underset{OSO_3Na}{CH}—CH_3$
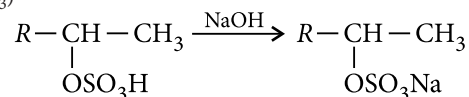
The end product is a
(a) soap   (b) fertiliser
(c) preservative   (d) detergent.

38. Which of the following statements is correct when a chain transfer agent is added to vinyl polymerisation process?

(a) Polymerisation occurs at the same rate whether chain transfer agent is present or not.
(b) The polymer formed has lower average molecular mass.
(c) The polymer formed contains small amounts of chlorine.
(d) All of these.

39. Bleeding is stopped by the application of ferric chloride because
(a) the blood starts flowing in the opposite direction
(b) the blood reacts and a solid is formed which seals the blood vessel
(c) the blood is coagulated and the blood vessels are sealed
(d) the ferric chloride seals the blood vessel.

40. (Complex-A) $\longleftarrow$ Metal ion with $\longrightarrow$ (Complex-B)
t_{2g}^3, e_g^1 d^n configuration t_{2g}^4, e_g^0

Complex-A and complex-B are respectively
(a) $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{4-}$
(b) $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{4-}$
(c) $[Mn(H_2O)_6]^{2+}$ and $[Mn(CN)_6]^{3-}$
(d) $[Mn(H_2O)_6]^{3+}$ and $[Mn(CN)_6]^{3-}$

ASSERTION AND REASON

Directions : In the following questions (41-60), a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

41. **Assertion :** In BrF_3, axial fluorine atoms are bent towards the equatorial fluorine.
Reason : Repulsion of lone pairs on equatorial fluorine is stronger as compared to on axial fluorine.

42. **Assertion :** $SO_{2(g)}$ and $H_2S_{(g)}$ can be distinguished by lime water.
Reason : SO_2 acts as reducing as well as oxidising agent but H_2S is only reducing agent.

43. **Assertion :** Buffer system of carbonic acid and sodium bicarbonate is used for the precipitation of hydroxides of third group elements.
Reason : It maintains the pH to a constant value, about 6.4.

44. **Assertion :** Excessive use of chlorinated synthetic pesticides causes soil and water pollutions.
Reason : Such pesticides are non-biodegradable.

45. **Assertion :** The enthalpy of reaction remains constant in the presence of a catalyst.
Reason : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy, the difference in energy of reactant and product remains the same.

46. **Assertion :** $C_6H_5N_2^+Cl^-$ couples with $C_6H_5N(CH_3)_2$ but not with 2,6-dimethyl-N, N-dimethylaniline.
Reason : Due to steric inhibition of resonance, the p-position of the 2, 6-dimethyl-N, N-dimethyl-aniline is not sufficiently activated for coupling reaction.

47. **Assertion :** Glucose and fructose give the same osazone.
Reason : During osazone formation stereochemistry at C_1 and C_2 is destroyed and rest of the structure remains same.

48. **Assertion :** Polyamides are best used as fibres because of high tensile strength.
Reason : Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence, provide high tensile strength to polymers.

49. **Assertion :** On heating a solid for a longer time, radiations become blue and then white as the temperature becomes very high.
Reason : Radiations emitted go from a higher frequency to lower frequency as the temperature increases.

50. **Assertion :** *Ortho*-hydroxybenzoic acid is much more acidic than benzoic acid.
Reason : Anion formed from *ortho*-hydroxy benzoic acid is destabilised by hydrogen bonding.

51. **Assertion :** Cycloalkenes decolourise the purple colour of dilute and cold $KMnO_4$ or red colour of bromine in carbon tetrachloride.
Reason : Cycloalkenes undergo the electrophilic addition reactions which are characteristic of alkenes.

52. **Assertion :** Friedel–Crafts reaction between benzene and acetic anhydride in the presence of anhydrous $AlCl_3$ yields acetophenone and not polysubstituted products.

Reason : Acetophenone formed poisons the catalyst, preventing further reaction.

53. **Assertion :** Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.
Reason : The reaction follows S_N1 mechanism.

54. **Assertion :** The rate of effusion of O_2 is less than that of N_2.
Reason : Molecular size of nitrogen is smaller than oxygen.

55. **Assertion :** The mobility of sodium ion is lower than that of potassium ion in aqueous solution.
Reason : The ionic mobilities depend upon the radius of the hydrated ion.

56. **Assertion :** The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.
Reason : Hydrogen sulphide is a weak acid.

57. **Assertion :** Ionic radii of Ta and Nb are same.
Reason : The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements.

58. **Assertion :** Both hypophosphoric acid and isohypophosphoric acid have same composition $H_4P_2O_6$ but their properties are different.
Reason : Due to different structural arrangement, their basicity, oxidation number of P atoms and reducing property are different.

59. **Assertion :** A mixture of noble gases can be separated by using coconut charcoal.
Reason : Activated coconut charcoal adsorbs different noble gases at different temperatures.

60. **Assertion :** $[Co(NO_3)_3(NH_3)_3]$ does not show optical isomerism.
Reason : It has a plane of symmetry.

SOLUTIONS

1. **(a) :** From van der Waals' equation,
$$\left[P + \frac{an^2}{V^2} \right](V - nb) = nRT \qquad \dots \text{(i)}$$

$\because \quad Z = \dfrac{PV}{nRT}$; if $Z > 1$, then $PV > nRT$

Which is possible from eq. (i) when $\dfrac{a}{V^2}$ is negligible, *i.e.*, $P(V - b) = RT$ \qquad [For $n = 1$]

or \quad $PV = RT + Pb$ \quad or $PV > RT$

or \quad $\dfrac{PV}{RT} > 1 \Rightarrow Z > 1$

2. **(d) :** $Al + \dfrac{3}{2}O_2 \longrightarrow \dfrac{1}{2}Al_2O_3$; $\Delta H = -837.8 \text{ kJ mol}^{-1}$
\qquad 27 g \qquad\qquad\qquad 51 g

(a) 1 mol of Al on combustion gives = 837.8 kJ of heat

$\therefore$ \quad 0.624 mol of Al on combustion will give
$= 837.8 \times 0.624 = 523$ kJ of heat.

(b) Formation of $\dfrac{1}{2}$ mole of Al_2O_3 gives = 837.8 kJ of heat

$\therefore$ \quad Formation of 0.624 mol of Al_2O_3 will give
$= 837.8 \times 2 \times 0.624 = 1045$ kJ of heat.

(c) 0.312 mol of Al on combustion will give
$= 837.8 \times 0.312 = 261$ kJ of heat.

(d) Formation of 0.150 mol of Al_2O_3 will give
$837.8 \times 2 \times 0.150 = 251.3$ kJ of heat.

3. **(c) :**
$$CuSO_4 \cdot 5H_2O + 2KI \longrightarrow K_2SO_4 + CuI_2 + 5H_2O] \times 2$$
$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$
$$\overline{2CuSO_4 \cdot 5H_2O + 4KI \longrightarrow 2K_2SO_4 + Cu_2I_2 + I_2 + 10H_2O}$$

Eq. wt. of $CuSO_4 \cdot 5H_2O$ = Mol. wt./1 = 250
At equivalence point,
No. of gram equivalents of hypo
\qquad = No. of gram equivalents of $CuSO_4.5H_2O$

$\Rightarrow \quad \dfrac{100}{1000} \times 0.1 = \dfrac{x}{\text{eq. wt.of } CuSO_4.5H_2O}$

$\Rightarrow \quad x = 0.01 \times 250 = 2.5$ g

4. **(a) :** Corey-House synthesis involves S_N2 attack of lithium dialkylcuprate on alkyl halide, therefore, proceeds better with a primary halide.

5. **(d) :**

6. (a) : For the reaction,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta n_g = 2 - 1 = 1$$

(a) According to Le Chatelier's principle, with the decrease of pressure, reaction shifts towards right, *i.e.*, proportion of NO_2 increases. Statement (a) is correct.

(b) Value of K increases with increase of temperature and hence, reaction is endothermic, *i.e.*, $\Delta H = +$ve.

Hence, statement (b) is incorrect.

(c) $K_p = \dfrac{[p_{NO_2}]^2}{[p_{N_2O_4}]} = \dfrac{atm^2}{atm} = atm$

Hence, statement (c) is incorrect.

(d)
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
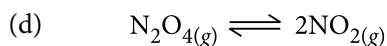
Initial: 1   0
At eq.: $1 - \alpha_1$ $2\alpha_1$

$$K_p = \frac{(2\alpha_1)^2}{1 - \alpha_1} = 1.7 \times 10^3 \text{ at 500 K}$$

$$4\alpha_1^2 = 1.7 \times 10^3$$

$$[\because (1 - \alpha_1 \approx 1), \text{ since } \alpha \text{ is small}]$$

$$\alpha_1 = \sqrt{\frac{1.7 \times 10^3}{4}}$$

$$\alpha_1 = 0.206 \times 10^2$$

Initially the pressure was 1 atm, now let it be 2 atm (100% increase).

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
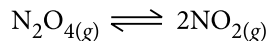
Initial: 2   0
At eq.: $2 - \alpha_2$ $2\alpha_2$

$$K_p = \frac{(2\alpha_2)^2}{2 - \alpha_2} = 1.7 \times 10^3 \text{ at 500 K}$$

$$\frac{4\alpha_2^2}{2} = 1.7 \times 10^3 \quad [\because (2 - \alpha_2 \approx 2), \text{ since } \alpha \text{ is small}]$$

$$\alpha_2 = \sqrt{\frac{1.7 \times 10^3}{2}}$$

$$\frac{\alpha_2}{\alpha_1} = \sqrt{\frac{1.7 \times 10^3 \times 4}{2 \times 1.7 \times 10^3}} = \sqrt{2} = 1.4$$

∴ When the pressure is increased by 100% the increase in α is 1.4 times (which is not 50%). Hence, statement (d) is incorrect.

7. (d) : 11.2 volume $H_2O_2 = 1$ M

10 volume $H_2O_2 = \dfrac{10}{11.2}$ M

15 volume $H_2O_2 = \dfrac{15}{11.2}$ M

20 volume $H_2O_2 = \dfrac{20}{11.2}$ M

$$M_f \times V_f = M_1V_1 + M_2V_2 + M_3V_3 + M_4V_4$$

$$M_f \times 3 = \frac{10 \times 0.5}{11.2} + \frac{15 \times 0.5}{11.2} + \frac{20 \times 0.5}{11.2} + zero(\text{For } H_2O)$$

$$M_f = \frac{7.5}{11.2}$$

1 M H_2O_2 has volume strength 11.2

$\dfrac{7.5}{11.2}$ M H_2O_2 will have volume strength

$$= 11.2 \times \frac{7.5}{11.2} = 7.5$$

8. (a) : Small sized cations have strong complex formation tendency with ligands either simple or chelating.

9. (a) : The spontaneous reactions also require certain amount of activation energy, therefore, heating is required.

10. (b) : There is partially filled $3d$ subshell, it forms a coloured ion and a complex compound. It has high melting point since it is a metal, forms strong metallic bonds.

11. (a) :

	$ZnCl_2$ <	$SnCl_2$ <	SO_4^{2-}
Hybridisation :	sp	sp^2	sp^3
p-Character :	50%	66.6%	75%
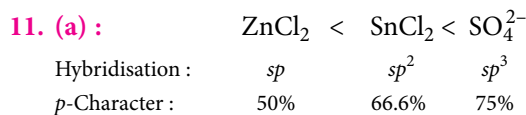
12. (b) : The driving force behind this reaction is the formation of six membered ring.
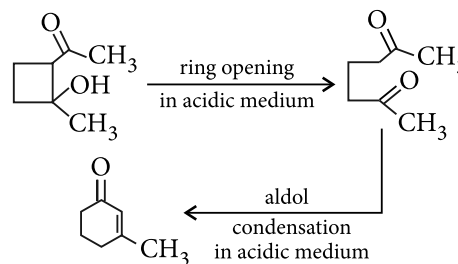
13. (c) : $P'_A = P_A^\circ \cdot X_A = P_M \cdot Y_A$

$P'_B = P_B^\circ \cdot X_B = P_M \cdot Y_B$

where P_M = partial pressure of the mixture

$$\therefore \quad \frac{P_A^\circ \, X_A}{P_B^\circ \, X_B} = \frac{Y_A}{Y_B}$$

$$\therefore \quad \frac{P_A^\circ}{P_B^\circ} > 1 \qquad \therefore \quad \frac{X_A}{X_B} > \frac{Y_A}{Y_B}$$

14. (c) : Since rate constant = 1.0×10^7 mol L^{-1} sec^{-1}

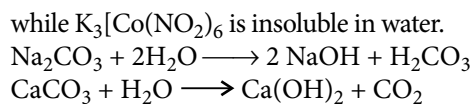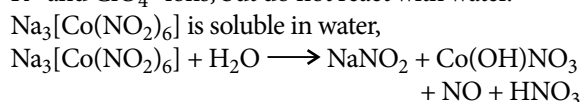For zero order, $t = \dfrac{x}{k} = \dfrac{\text{concentration used}}{\text{rate constant}}$ ...(i)

0.05 mL (of a drop) has 3×10^{-6} mole of H$^+$.

∴ 1000 mL will have $\dfrac{3 \times 10^{-6} \times 10^3}{0.05}$ mole of H$^+$

$= 0.06$ mol L^{-1} of H$^+$

By eqn. (i), $t = \dfrac{0.06}{1 \times 10^7} = 6 \times 10^{-9}$ sec

15. (d) : NaClO$_4$ is soluble in water,

NaClO$_4$ + H$_2$O $\longrightarrow$ NaOH + HClO$_4$

while KClO$_4$ is insoluble in water, it dissociates into K$^+$ and ClO$_4^-$ ions, but do not react with water.

Na$_3$[Co(NO$_2$)$_6$] is soluble in water,

Na$_3$[Co(NO$_2$)$_6$] + H$_2$O $\longrightarrow$ NaNO$_2$ + Co(OH)NO$_3$ + NO + HNO$_3$

while K$_3$[Co(NO$_2$)$_6$ is insoluble in water.

Na$_2$CO$_3$ + 2H$_2$O $\longrightarrow$ 2 NaOH + H$_2$CO$_3$

CaCO$_3$ + H$_2$O $\longrightarrow$ Ca(OH)$_2$ + CO$_2$
                              Insoluble

NaCl as well as CaCl$_2$ are soluble in water and their solubility increases with rise in temperature.

16. (d) : Among the given compounds, phenol (IV) has least molar mass and therefore, possesses least boiling point. Among the three isomeric phenols, catechol (I) forms intramolecular H-bonding leading to lowest boiling point. On the other hand, resorcinol (II) and hydroquinone (III) do not undergo chelation, hence, they will involve in extensive intermolecular H-bonding leading to higher boiling points. Further, intermolecular H-bonding is stronger in the *p*-isomer than the *m*-isomer hence, former has highest boiling point. Thus, the decreasing order of boiling points is III > II > I > IV.

17. (d)

18. (c) : At equilibrium both the solutions have same vapour pressure as well as same concentrations because both the solutes are non-electrolyte. Suppose *w* g water is transferred from dilute solution to concentrated solution, then

$C_1 = C_2$ or $\dfrac{w_1}{M_1 V_1} = \dfrac{w_2}{M_2 V_2}$

and, volume of solvent

≈ volume of solution (for dilute solutions)

∴ $\dfrac{20}{\dfrac{342 \times (100 + w)}{1000 \times d}} = \dfrac{10}{\dfrac{342 \times (100 - w)}{1000 \times d}}$

(d = density of water)

∴ $\dfrac{20}{100 + w} = \dfrac{10}{100 - w} \Rightarrow w = 33.3$ g

19. (b) : Element *Y* can probably be tin which conducts electricity and belongs to group 14. SnCl$_4$ is a colourless volatile liquid whereas SnCl$_2$ is a colourless solid.

20. (d) : Elemental bromine cannot convert acid to acid bromide. So, (a) and (b) are incorrect choices. In addition elimination reactions across the double bond for halogens (bromine here), first a cyclic bromonium ion is formed, which is attacked by the nucleophile, bromide (Br$^-$). But here we have a better nucleophile *i.e.*, a lone pair on the –OH group in the vicinity of the reaction centre. This attacks successfully before the bromide ion can approach in the second step.
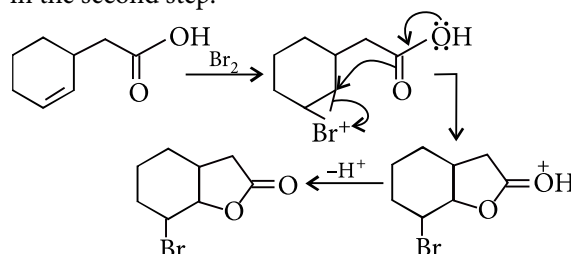
21. (a) : For the given cell, Zn + Cu^{2+} $\longrightarrow$ Zn^{2+} + Cu

$E_{\text{Cell}} = E^{\circ}_{\text{Cell}} - \dfrac{0.059}{2} \log \dfrac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$

∴ $E_1 = E^{\circ}_{\text{Cell}} - \dfrac{0.059}{2} \log \dfrac{0.01}{1.0} = E^{\circ} + 0.059$

∴ $E_2 = E^{\circ}_{\text{Cell}} - \dfrac{0.059}{2} \log \dfrac{1.0}{0.01} = E^{\circ} - 0.059$

∴ $E_1 > E_2$

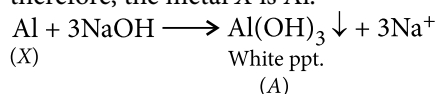**22. (b) :** Average rate during the time interval 30-60 s.

Rate $= -\dfrac{C_2 - C_1}{t_2 - t_1} = -\dfrac{(0.17 - 0.31)}{60 - 30} = \dfrac{0.14}{30}$

$= 4.67 \times 10^{-3}$ mol L^{-1} s^{-1}

23. (d) : In HgI$_3^-$, Hg^{2+} ion is present having electronic configuration $5d^{10}6s^0$.

Hybridisation ∴ sp^2 (trigonal planar).

All electrons are paired, hence, diamagnetic.

24. (d) : Since, metal *X* on treatment with sodium hydroxide gives white precipitate which dissolves in excess of NaOH to give soluble complex (*B*), therefore, the metal *X* is Al.

Al + 3NaOH $\longrightarrow$ Al(OH)$_3$ $\downarrow$ + 3Na$^+$
(*X*)   White ppt.
                              (*A*)

$$\underset{(A)}{Al(OH)_3} + \underset{(Excess)}{NaOH} \longrightarrow \underset{\substack{Sodium\ tetrahydroxoaluminate\ (III) \\ (B)}}{Na^+[Al(OH)_4]^-}$$

$$\underset{(A)}{Al(OH)_3} + 3HCl_{(aq)} \longrightarrow \underset{(C)}{AlCl_3} + 3H_2O$$

$$\underset{(A)}{2Al(OH)_3} \xrightarrow{\Delta} \underset{\substack{(D) \\ Alumina}}{Al_2O_3} + 3H_2O$$
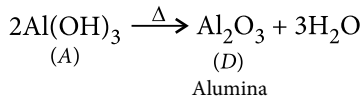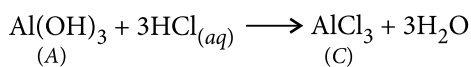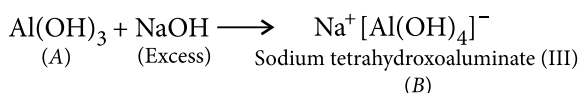
25. (a) : $-\overset{+}{N}H_2Cl$ is the most powerful deactivator amongst the following, followed by $-COCH_3$ and $-Cl$. On the other hand, $-NH_2$ and $-NHCOCH_3$ groups are activators but $-NH_2$ is a more powerful activator than $-NHCOCH_3$. Hence, the correct order is II < V < IV < III < I.

26. (a) : Excess of hydrochloric acid avoids the possibility of coupling reaction with aniline by suppressing the concentration of free aniline for coupling reaction.

27. (a) : Density of $fcc = \dfrac{Z_1 \times At.\ mass}{N_A \times a_1^3}$ and

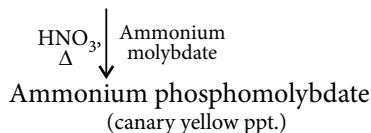Density of $bcc = \dfrac{Z_2 \times At.\ mass}{N_A \times a_2^3}$

$$\dfrac{d_{fcc}}{d_{bcc}} = \dfrac{Z_1}{Z_2} \times \dfrac{a_2^3}{a_1^3}$$
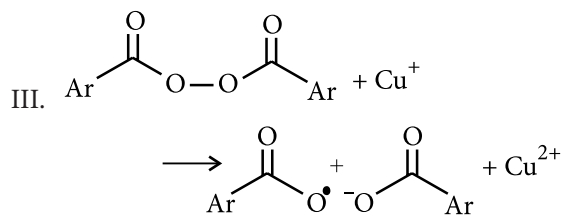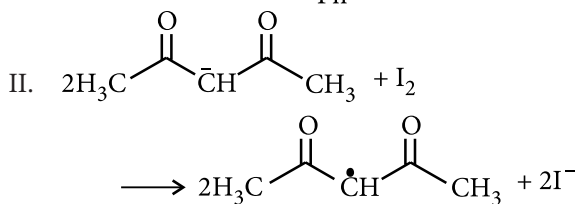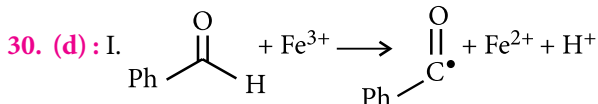
For fcc, $Z_1 = 4$; $a_1^3 = (3.5 \times 10^{-8})^3$

For bcc, $Z_2 = 2$; $a_2^3 = (3.0 \times 10^{-8})^3$

$$\dfrac{d_{fcc}}{d_{bcc}} = \dfrac{4 \times (3 \times 10^{-8})^3}{2 \times (3.5 \times 10^{-8})^3} = 1.259$$

28. (a) : $\underset{acid}{Orthophosphoric} \xrightarrow{AgNO_3} \underset{(yellow\ ppt.)}{Ag_3PO_4} + 3HNO_3$

$\Big\downarrow \overset{HNO_3,}{\underset{\Delta}{}} \substack{Ammonium \\ molybdate}$

$\underset{(canary\ yellow\ ppt.)}{Ammonium\ phosphomolybdate}$

29. (c) : $CHCl_3$ does not give free Cl^- ions to react with $AgNO_3$ due to strong $C-Cl$ bond whereas $C-I$ bond is relatively weaker. Thus, free I^- ions are available from CHI_3 to react with $AgNO_3$.

30. (d) : I.

II. $2H_3C\overset{O}{\underset{}{C}}\bar{C}H\overset{O}{\underset{}{C}}CH_3 + I_2$

$\longrightarrow 2H_3C\overset{O}{\underset{}{C}}\overset{\bullet}{C}H\overset{O}{\underset{}{C}}CH_3 + 2I^-$

III. $\underset{}{Ar}\overset{O}{\underset{}{C}}O-O\overset{O}{\underset{}{C}}Ar + Cu^+$

$\longrightarrow \underset{}{Ar}\overset{O}{\underset{}{C}}\overset{+}{O^{\bullet}}\ ^-O\overset{O}{\underset{}{C}}Ar + Cu^{2+}$

31. (b) : $\Lambda^{\circ}_{(CH_3COOH)}$

$= (\lambda^{\circ}_{CH_3COO^-} + \lambda^{\circ}_{Na^+}) + (\lambda^{\circ}_{H^+} + \lambda^{\circ}_{Cl^-})$
$\qquad\qquad\qquad - (\lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-})$

$= 90 + 425 - 125 = 390$ mho cm^2 mol^{-1}

Degree of dissociation $= \dfrac{\Lambda_m}{\Lambda^{\circ}_m} = \dfrac{7.8}{390} = 0.02$
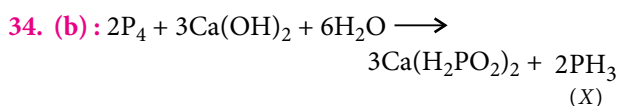
32. (a) : In acidic medium, MnO_4^- reduces into Mn(II), which catalyses the reaction.

33. (c) : (I) Four unpaired electrons
(II) Three unpaired electrons
(III) Five unpaired electrons
(IV) One unpaired electron

34. (b) : $2P_4 + 3Ca(OH)_2 + 6H_2O \longrightarrow$

$$3Ca(H_2PO_2)_2 + \underset{(X)}{2PH_3}$$

(A) is H_3PO_2 (hypophosphorous acid), a monobasic acid. PH_3 is less basic than NH_3. The bond angle in (X) is less than that present in NH_3, H_3PO_2 on heating gives orthophosphoric acid and phosphine (X).
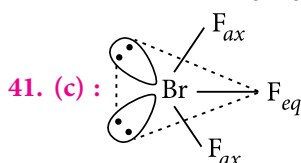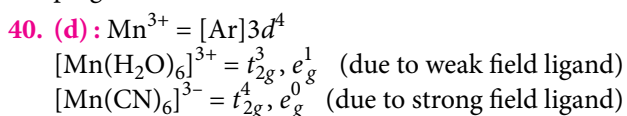
35. (c) :
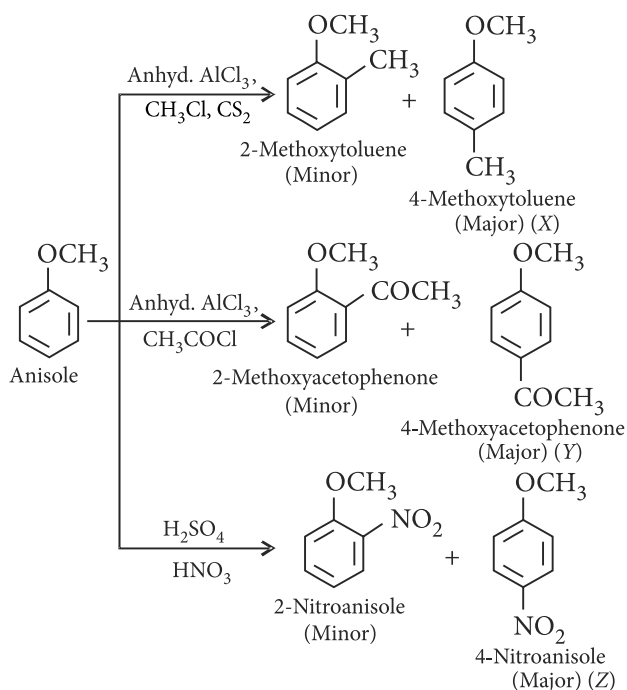
36. (b)

37. (d) : Detergents are sodium salts of long chain sulphonic acids.

38. (d)

39. (c) : Fe^{3+} ions coagulate the soluble proteins (present in blood plasma) which are negatively charged. Remember that when a blood vessel breaks, bleeding stops by itself after sometime. It is due to clustering together of platelets to form a plug.

40. (d) : $Mn^{3+} = [Ar]3d^4$
$[Mn(H_2O)_6]^{3+} = t_{2g}^3, e_g^1$ (due to weak field ligand)
$[Mn(CN)_6]^{3-} = t_{2g}^4, e_g^0$ (due to strong field ligand)

41. (c) :

Axial fluorine atoms are bent towards the equatorial fluorine in order to minimise the lp-lp repulsion.

42. (b) : $SO_2 + Ca(OH)_2 \longrightarrow \underset{\text{(White ppt.)}}{CaSO_3} + H_2O$
$H_2S + Ca(OH)_2 \longrightarrow$ No ppt.
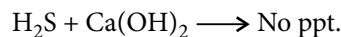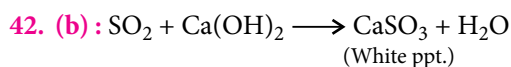
43. (d) : Buffer system of carbonic acid and sodium bicarbonate is found in our blood. It maintains the pH of blood to a constant value of about 7.4.

44. (a) : Pesticides being non-biodegradable result in soil as well as water pollutions.

45. (a)   46. (a)   47. (a)   48. (a)

49. (d) : As the temperature increases, radiations emitted go from lower to higher frequency. Thus, on heating a solid for a longer time, radiations become white and then blue as the temperature becomes very high.

50. (c) : Anion formed from *ortho*-hydroxybenzoic acid is stabilised by hydrogen bonding.

51. (a) :
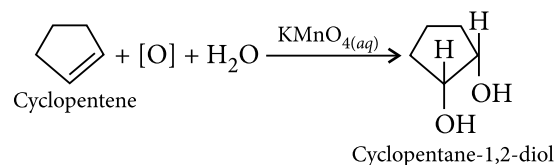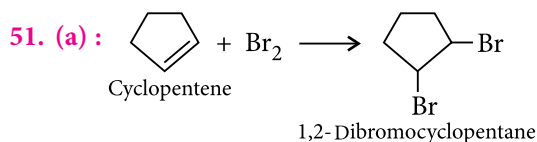
52. (c) : Acylation introduces a deactivating group on benzene ring (*i.e.*, $R-\overset{O}{\underset{||}{C}}-$ group), thus, further reaction does not take place.

53. (a)

54. (c) : Molecular size of O_2 is smaller than N_2.

55. (a)

56. (b) : In the presence of hydrochloric acid, the ionisation of hydrogen sulphide is suppressed due to common ion effect.

57. (a)

58. (a) : Isohypophosphoric acid is an isomeric form of hypophosphoric acid. It has different structure having non-identical P-atoms.

59. (a)   60. (a)

◈◈

ACYCLIC HYDROCARBONS
(Open chain structures containing C and H only)

CONCEPT MAP

Although hydrocarbons are primarily consumed in fuels, non-fuel applications of hydrocarbons are of great importance to society and the economy. Certain hydrocarbons can be found in lubricating oils, greases, solvents, fuels, wax, asphalts, cosmetics and plastics.

Class XI **Class XII**

THE SOLID STATE

CONCEPT MAP

The solid state chemistry covers the latest advances in advanced inorganic materials with applications ranging from energy storage systems, electronic materials and sensors to the more traditional, but increasingly hi-tech materials and industries that include glass, cement and refractories.

Saturated
C—C single bonds present

Unsaturated
C—C multiple bonds present

Alkanes
General formula, C_nH_{2n+2}

Preparation

- **From alkyl halides :**

$$2R{-}Br + 2Na \xrightarrow{\text{Dry ether}} R{-}R + 2NaBr$$
(Wurtz reaction)

$R{-}X$ can be converted to alkane using $Zn + CH_3COOH$, Zn + dil. HCl, Zn–Cu + C_2H_5OH, $LiAlH_4$, Zn + NaOH, $NaBH_4$ and Ph_3SnH reducing agents.

- **From carboxylic acids :**

$$RCOOH \xrightarrow{\text{Red P/HI}} RCH_3 + H_2O + I_2$$

$$2RCOONa + NaOH \xrightarrow{\Delta} Na_2CO_3 + RH$$

$$2RCOOK + 2H_2O \xrightarrow{\text{Electrolysis}}$$
$$R{-}R + 2CO_2 + H_2 + 2KOH$$
(Kolbe's electrolysis method)

- **From carbonyl compounds :**

$$RCOCH_3 \xrightarrow[C_2H_5ONa]{NH_2NH_2} R{-}CH_2CH_3$$
(Wolff-Kishner reduction)

$$RCOCH_3 \xrightarrow[\text{conc. HCl}]{Zn/Hg} RCH_2CH_3 + H_2O$$
(Clemmensen reduction)

Properties

- **Substitution reaction :**

$$CH_3CH_2CH_3 \xrightarrow{Cl_2} \begin{cases} CH_3CH_2CH_2Cl \\ CH_3{-}CH{-}CH_3 \\ \quad\quad | \\ \quad\quad Cl \end{cases}$$

Order of reactivity :
Alkanes : $3° > 2° > 1° > CH_4$
Halogens : $F_2 > Cl_2 > Br_2 > I_2$

- **Oxidation :**
(a) Combustion or complete oxidation :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow$$
$$nCO_2 + (n+1)H_2O + \text{heat}$$

(b) Catalytic oxidation :

$$2CH_4 + O_2 \xrightarrow[\text{100 atm / 473K}]{\text{Cu-tube}} 2CH_3OH$$
$$9 \quad : \quad 1$$

Alkenes ($\,{>}C{=}C{<}$)
General formula, C_nH_{2n}

Preparation

- **Hydrogenation of alkynes :**
(a) $R{-}C{\equiv}C{-}R' + H_2$

$$\xrightarrow[\text{(Lindlar's catalyst)}]{\text{Pd/C}} \underset{H}{\overset{R}{>}}C{=}C\underset{H}{\overset{R'}{<}}$$
(cis-alkene)

(b) $R{-}C{\equiv}C{-}R' + H_2$

$$\xrightarrow[\text{or LiAlH}_4]{\text{Na/liq. NH}_3} \underset{H}{\overset{R}{>}}C{=}C\underset{R'}{\overset{H}{<}}$$
(trans-alkene)

- **Dehydrohalogenation :**

$$\underset{H}{\overset{H}{|}}\underset{|}{C}\overset{\beta}{}\underset{\alpha}{\overset{H}{|}}\underset{X}{\overset{|}{C}}{-}H \xrightarrow[\Delta]{\text{alc. KOH}} \underset{H}{\overset{H}{>}}C{=}C\underset{H}{\overset{H}{<}}$$
(β-elimination)

- **Dehalogenation :**

$$X{-}CH_2{-}CH_2{-}X + Zn \xrightarrow[\Delta]{\text{Methanol}}$$
(vic. dihalides)
$$CH_2{=}CH_2 + ZnX_2$$

- **Dehydration of alcohols :**

$$CH_3CH_2{-}OH \xrightarrow[\Delta]{\text{Conc. H}_2SO_4}$$
$$CH_2{=}CH_2$$

Properties

- **Addition of halogen :**

$$CH_2{=}CH_2 + Br_2 \xrightarrow{CCl_4} \begin{matrix} CH_2{-}Br \\ | \\ CH_2{-}Br \end{matrix}$$
(Brown colour)   (Colourless)

- **Addition of halogen acid :**

$$CH_3{-}CH{=}CH_2 + HBr \xrightarrow{\text{Markownikoff's rule}}$$
$$\begin{matrix} Br \\ | \\ CH_3{-}CH{-}CH_3 \end{matrix}$$

HBr addition in presence of peroxide follows *anti-Markownikoff's rule*, known as *Kharasch effect* or *peroxide effect*.

- **Oxidation :**

$$CH_2{=}CH_2 + H_2O + O \xrightarrow[\text{298-303 K}]{\text{alk. KMnO}_4}$$
$$HO{-}CH_2{-}CH_2{-}OH$$

Alkynes (—C≡C—)
General formula, C_nH_{2n-2}

Preparation

- **From calcium carbide :**

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

- **Dehalogenation :**

$$\begin{matrix} CH_2{-}CH_2 \\ |\quad\quad| \\ Br\quad Br \end{matrix} \xrightarrow{KOH} CH_2{=}CHBr$$

$$\xrightarrow{NaNH_2} CH{\equiv}CH$$

Properties

- **Acidic nature :**
$$CH{\equiv}CH + Na \xrightarrow{\text{liq. NH}_3} CH{\equiv}\bar{C}\overset{+}{N}a + \tfrac{1}{2}H_2$$

- **Addition reactions :**
$$CH{\equiv}CH \xrightarrow[H_2]{\text{Pt/Pd/Ni}} CH_3{-}CH_3$$

$$CH_3{-}C{\equiv}CH \xrightarrow[CCl_4]{Br_2}$$
$$CH_3{-}CBr_2{-}CHBr_2$$

$$CH_3{-}C{\equiv}CH \xrightarrow{H_2O} CH_3{-}\underset{OH}{\overset{|}{C}}{=}CH_2$$

$$\xrightarrow{\text{Isomerisation}} CH_3{-}\underset{O}{\overset{|\,|}{C}}{-}CH_3$$

Commercial Uses

- **Alkanes :** Ethane is used for making hexachloroethane which is an *artificial camphor*. Higher alkanes in the form of gasoline, kerosene oil, diesel, lubricating oils and paraffin wax are widely used.

- **Alkenes :** Ethene is used as a general anaesthetic. It is a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc.

- **Alkynes :** Acetylene is used as a general anaesthetic under the name *naracylene*. Acetylene is used as an illuminant.

Classification based on Crystal Lattice

SOLIDS

Classification based on Magnetic Properties

Crystalline Solids

- True solids.
- Anisotropic.
- Have definite pattern of arrangements of atoms, ions or molecules.
- Exhibit plane, axis and centre of symmetry.
- Long range order.
- Are categorised according to intermolecular forces into : Molecular, ionic, metallic and covalent solids.

Amorphous Solids

- Isotropic.
- Pseudo solids or supercooled liquids.
- Do not have a definite pattern of arrangement.
- Short range order.
- Do not show any symmetry.

Primitive Unit Cells
- Constituent particles are present only at the corners of the unit cell.
- Consist of 7 types of arrangements with cubic as most symmetric and triclinic as least symmetric.

- **Diamagnetic Substances :** Substances which are weakly repelled by external magnetic field, *e.g.*, N_2, NaCl, Zn, TiO_2, etc.
- **Paramagnetic Substances :** Substances which are weakly attracted by external magnetic field, *e.g.*, O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}, etc.
- **Ferromagnetic Substances :** Substances which show permanent magnetism even in the absence of external magnetic field, *e.g.*, Ni, Fe, Co, etc.
- **Antiferromagnetic Substances :** Substances which have zero net dipole moment even though they have large number of unpaired electrons, *e.g.*, MnO.
- **Ferrimagnetic Substances :** These are the substances which possess very small net magnetic moment even though they have large number of unpaired electrons, *e.g.*, Fe_3O_4.

Crystal Lattice and Unit Cells

Centred Unit Cells
Constituent particles are present at the corners and at :
- the centre of the unit cell (*bcc*)
- the centre of each face of the unit cell (*fcc*)
- the centre of any two opposite faces (End-centred)

Cubic System

$$d = \frac{Z \times M}{a^3 \times N_A}\,\text{g cm}^{-3}$$

Type	Simple cubic	*bcc*	*fcc*
Z	$8 \times \frac{1}{8} = 1$	$8 \times \frac{1}{8} + 1 \times 1 = 2$	$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
C. No.	6	8	12
Relation of r, d & a	$r = \frac{d}{2} = \frac{a}{2}$ since $d = a$	$r = \frac{d}{2} = \frac{a}{2\sqrt{2}}$ since $d = \frac{a}{\sqrt{2}}$	$r = \frac{d}{2} = \frac{\sqrt{3}a}{4}$ since $d = \frac{\sqrt{3}a}{2}$
Packing Efficiency	52.4%	68%	74%

Voids

Type	Size	No. of Voids
Octahedral	0.414 R	N
Tetrahedral	0.225 R	$2N$

Types of Defects

Non-stoichiometric Defect
Arises due to the presence of constituent particles in non-stoichiometric ratio.

Stoichiometric Defect
(Intrinsic or Thermodynamic Defect)
Does not disturb the stoichiometry of solid.

Frenkel Defect
- It is due to missing of ions (usually cations) from the lattice sites and these occupy interstitial sites.
- It has no effect on the density of crystal.
- This is found in crystal with low coordination no. *e.g.*, AgI, ZnS, etc.

Schottky Defect
- It is due to equal no. of cations and anions missing from lattice sites.
- It results in decrease in density of crystal.
- This is found in the highly ionic compounds having cation and anion of same size, *e.g.*, NaCl, CsCl, etc.

Metal Excess Defect : Arises due to anionic vacancies, leaving a hole which is occupied by an electron thus, maintaining electrical balance. The anionic sites, occupied by unpaired electrons, are called F-centres and these impart colour to crystals.

Metal Deficiency Defect : Arises when metal shows variable valency *i.e.*, in transition metals. The defect occurs due to missing of a cation from its lattice site and the presence of the cation having higher charge in the adjacent lattice site.

ADVANCED CHEMISTRY BLOC

(THE WAVE THEORY OF THE ATOM)

Mukul C. Ray, Odisha

PARTICLES AND WAVES

According to wave theory of light, refraction and diffraction can be explained by the properties of waves. Other properties of light such as the origin of line spectra and the photoelectric effect need a particle or photon theory for their explanation. The success of the dual theory of light led Louis de Broglie (pronounce as de Broy) to speculate in 1924 on whether particles might have wave properties. He made the bold suggestion that electrons have wave properties as well as the properties of particles. Erwin Schrödinger used this model to work out a wave theory of the atom.

Significance of ψ

For electromagnetic wave, the intensity of radiation at any point is proportional to the square of the amplitude of the wave at that point. Again, greater the intensity of radiation at a point, greater is the number of photons striking that point. This means, greater the amplitude of light wave at a point, greater is the probability of a photon to be found there.

Parallel arguments may be applied to matter waves, *i.e.*, the probability of finding the electrons at a point is proportional to ψ^2.

Any equation for a standing wave must obey certain conditions :

◯ Standing wave should have zero amplitude at two ends.

◯ In addition,

  • ψ must be single-valued
  • ψ must be finite and continuous
  • ψ must be square integrable *i.e.,*

$$\int_{-\infty}^{+\infty} \psi^2 dxdydz = 1$$

The total probability of finding the electrons over the whole space must be equal to 1 *i.e.*, ψ must be normalised.
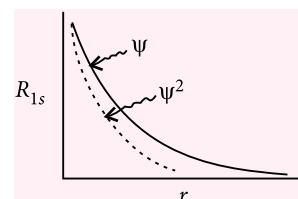
Radial wave function ; *R*

The radial part of the wave function depends only on the value of '*n*' and '*l*'.

For 1*s*,

$$R = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{\frac{-Zr}{a_0}}$$

We know that the probability of finding a particle at some point is proportional to square of ψ. So, the dependence of probability on the radial distance from the nucleus will be obtained from the square of the radial part of the wave function *i.e.,* R^2.

We may consider the atom to be composed of concentric circles of thin shells of thickness *dr*. The volume *dV* of such a shell between *r* and *r* + *dr* may be readily calculated.

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

$$dV = 4\pi r^2 dr$$

The probability that an electron will be found in this volume is $R^2 dV$ or $4\pi r^2 R^2 dr$. The term $4\pi R^2 r^2$ is called the radial probability function or sometimes radial density function.
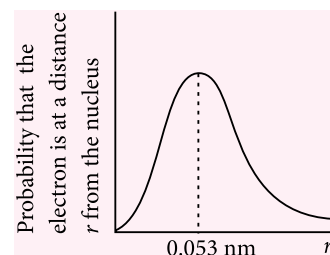
The maximum probability of finding the electron is at a distance of 0.053 nm. This is same as Bohr's calculation.

There is possibility that the electrons will be either closer to the nucleus or outside the nucleus of 0.053 nm. The probability of finding the electron decreases sharply, as the distance from the nucleus increases beyond $3r$. The volume of the space in which there is a 95% chance of finding the electrons is called the atomic orbital. On this model, the electron is not described as revolving in an orbit. The nucleus is described here as being surrounded by a three dimensional cloud of charge.

Penetration

The radial density of the $2s$-orbital spreads into the curve for the $1s$-orbital. The radial density of $3s$-orbital spreads into the $2s$ and $1s$-orbital and so on.

This is termed as penetration of orbitals, that is their distribution into inner core. As a consequence, an electron in outer orbital does not get the full screening by the inner electrons from the nuclear charge.
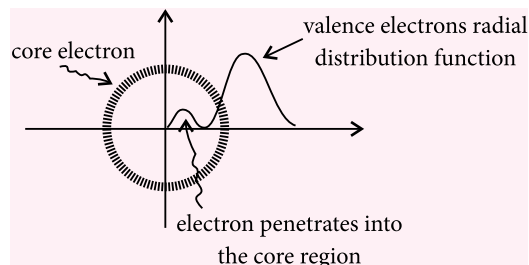
The enhanced nuclear charge does not change the basic shapes of the radial density curves, but their extension is reduced. This is called contraction of orbitals.
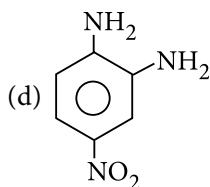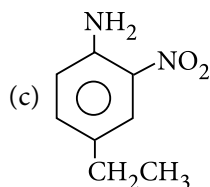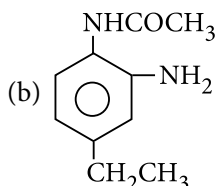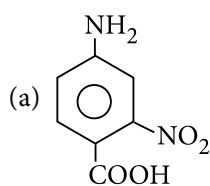
CONCEPT BOOSTER

Dear students, hope you all are fine. As I have always told, your learning process becomes abortive if it is not accompanied with practice. Make regular habit of practicing problems. This article 'Organic compounds containing nitrogen and its compounds (Amines and its salts)' will help you for that. Always set timer before solving a problem, then only you can get fruitful results.
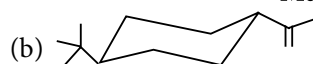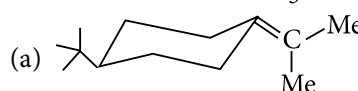
*Arunava Sarkar

1.
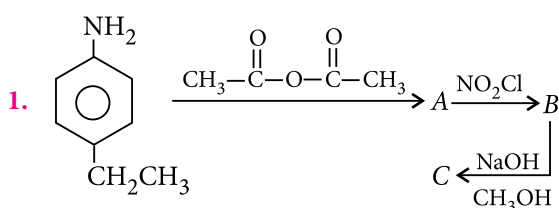
Identify 'C' in the above sequence of reactions.

(a)

(b)

(c)

(d)

2.

Identify the final product.

(a)

(b)

(c)

(d)

3.

(a)

(b)

(c)

(d) None of these

4.

(a)

(b)

(c)

(d) None of these

5.

(a)

(b)

*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

(c)

(d) None of these

(c)

(d)

6. $\xrightarrow[\text{2. dil. HCl}]{\text{1. Br}_2 + \text{KOH}}$?

(a)

(b)

(c)

(d) None of these

10. $\xrightarrow[\text{HCl,}]{\text{NaNO}_2}$ $\xrightarrow{\text{HPF}_6}$ $\xrightarrow{\Delta}$?
(0°C-5°C)

Identify the final product.

(a)

(b)

(c)
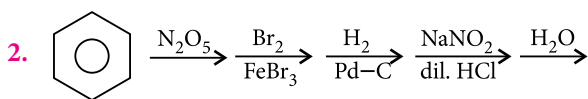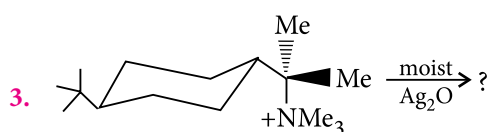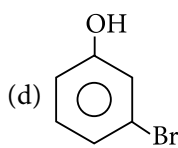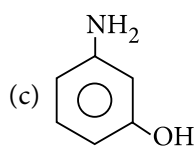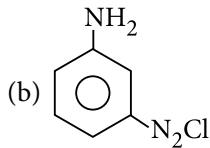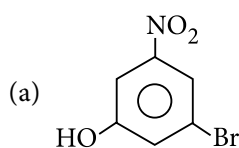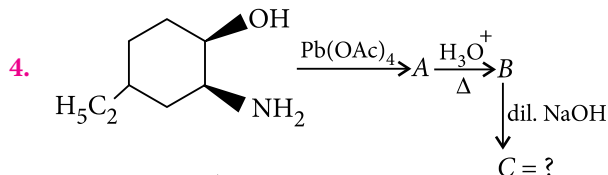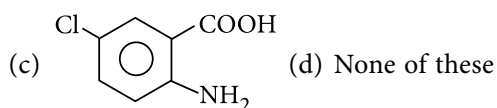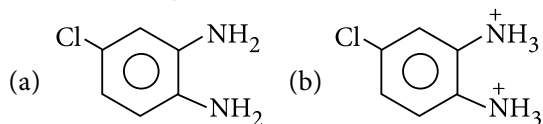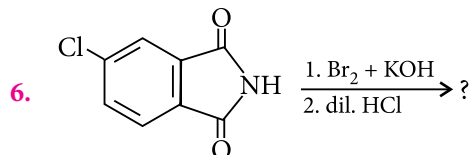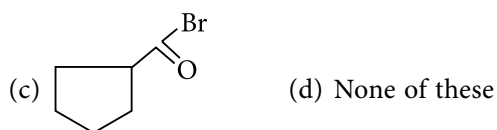
(d) None of these

7. Identify the major product in the following reaction :

 $\xrightarrow[\text{2. H}_2\text{O}]{\text{1. (CF}_3\text{CO)}_2\text{O} \quad \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3}$?

(a) Me—C—NH—◁ (b) ▷—C—NH—Me
$\quad\quad\;\;\overset{\|}{O}$ $\quad\quad\quad\quad\;\;\overset{\|}{O}$
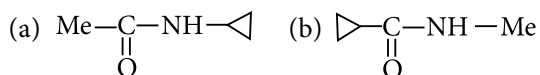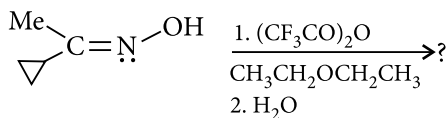
(c) both (a) and (b) are major and equally formed
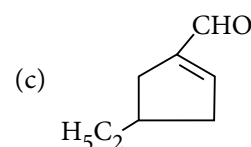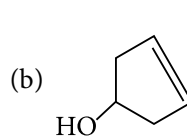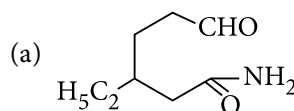
(d) Me—C—N—◁
$\quad\quad\overset{\|}{O}\;\overset{|}{F}$
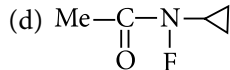
8. Arrange the following according to their increasing order of basicity :
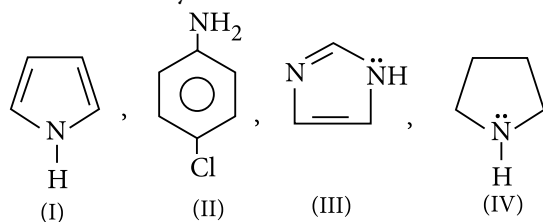
(a) I < II < III < IV (b) IV < III < II < I
(c) I > II < III > IV (d) None of these

9. $\xrightarrow[\text{H}_2\text{S}]{\text{NH}_3}$ $\xrightarrow[\text{dil. HCl}]{\text{NaNO}_2}$ $\xrightarrow[\text{KCN}]{\text{CuCN}}$ $\xrightarrow{\text{H}^+/\text{H}_2\text{O}}$ $\xrightarrow{\text{SOCl}_2}$?
(0°C-5°C)

Identify the final product.

(a)

(b)
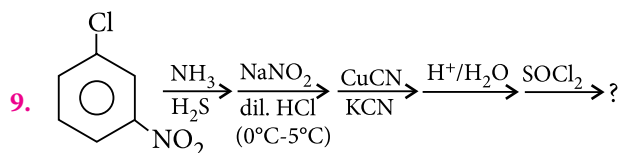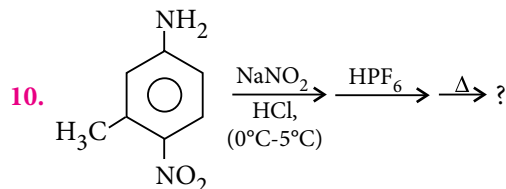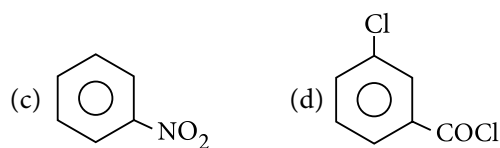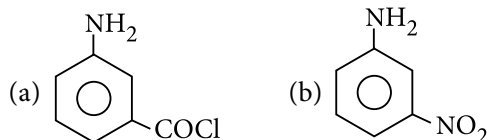
11. $\xrightarrow[\text{H}^+/\Delta]{\overset{O}{\text{CH}_3\overset{\|}{\text{C}}-\text{CH}_2-\text{CH}_2-\text{COOEt}}}$
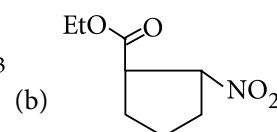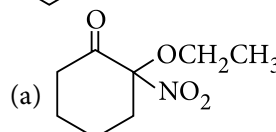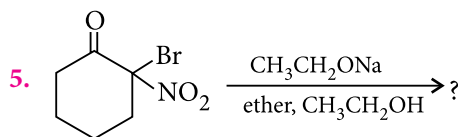
Identify the final product.

(a)

(b)

(c)
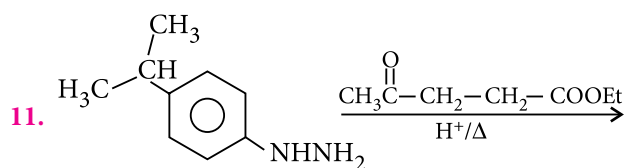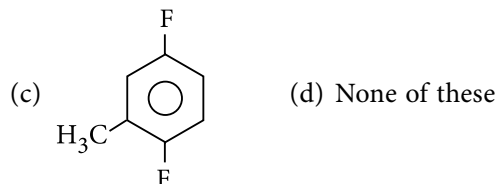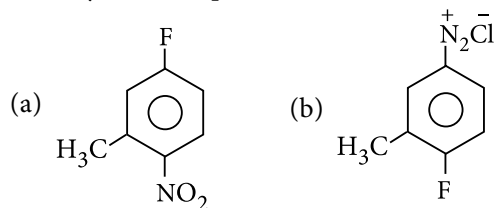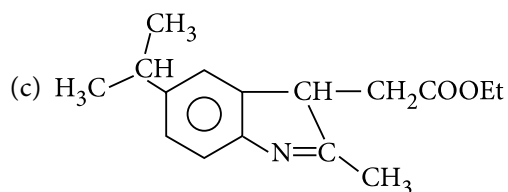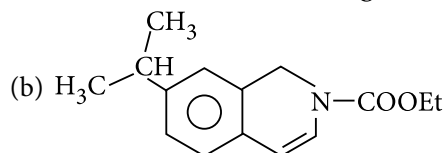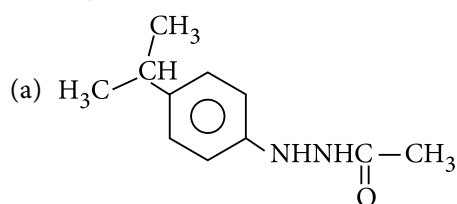
(d) None of these

SOLUTIONS

1. (c) : In presence of acetic anhydride, $-NH_2$ group is prone to be converted to $- NHCOCH_3$. NO_2Cl has polarisation as $\overset{\delta+}{N}O_2\overset{\delta-}{Cl}$. So, $\overset{+}{N}O_2$ will attack the ring activated by both $-NHCOCH_3$ and $-C_2H_5$ groups but being more powerful one, directive influence will be controlled by $- NHCOCH_3$, since, para position is blocked so, substitution will surely be at the ortho position. $NaOH/CH_3OH$ will convert $-NHCOCH_3$ back to $- NH_2$ as if hydrolysis taking place.

$\therefore$ Correct option is (c).

2. (d):
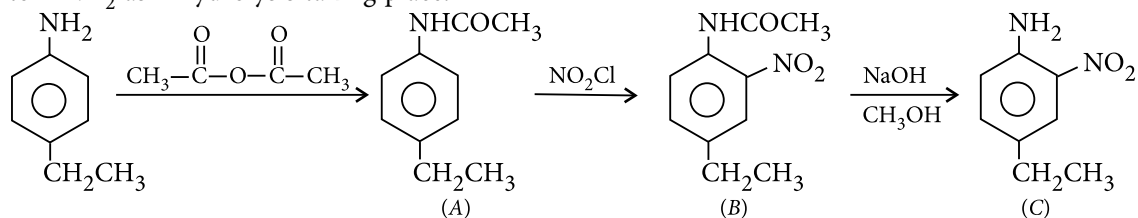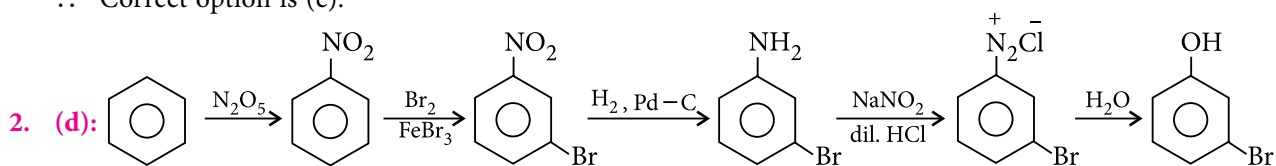
$-NO_2$ is meta directing. Hence, $-Br$ will be inserted at the meta positions.
$\therefore$ Correct option is (d).

3. (b): It is a mere case of Hoffmann's elimination. Moist Ag_2O ($Ag_2O + H_2O \longrightarrow 2AgOH$) will give $\overset{..}{O}H$ which will abstract proton from the less hindered site. Therefore, the reaction comes out to be as below :
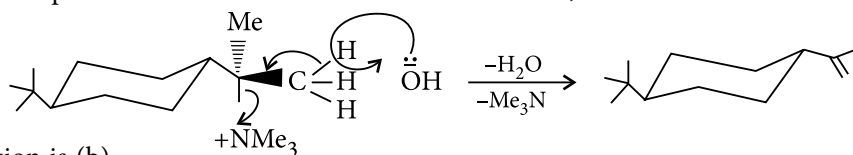
$\therefore$ Correct option is (b).

4. (c) : You know that $Pb(OAc)_4$ gives Criegee reaction. So, the first step will be as below along with the second step.
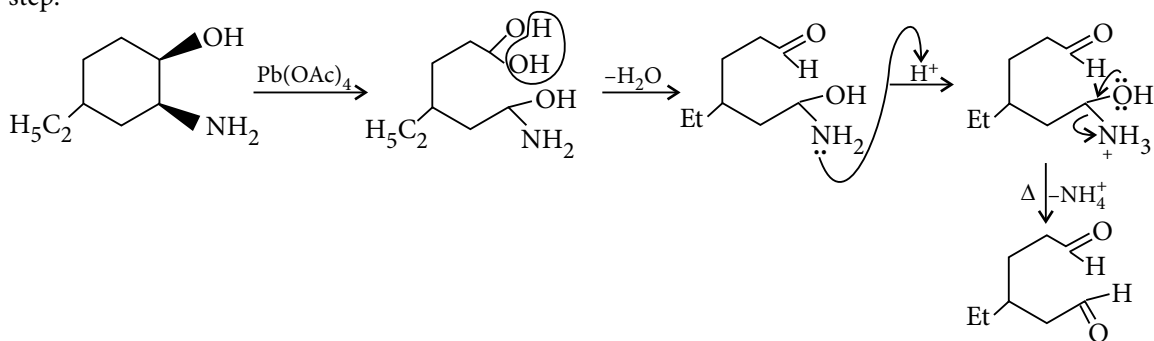
Now, in presence of dilute alkali, the product will undergo internal aldol condensation reaction as shown below :

$\therefore$ Correct option is (c).

5. (b):

CH₃CH₂Ö⁻ ... −Br⁻ ... CH₃CH₂Ö ... CH₃CH₂O—O⁻

CH₃CH₂O ... NO₂

EtO ... NO₂ ← CH₃CH₂O—H ← CH₃CH₂O ... NO₂

∴ Correct option is (b).

6. (c):

ÖH (−H₂O) elimination → ÖH addition →

−Br ← ÖH ← δ⁻ Br—Br δ⁺

Cl—COO⁻ N=C=O → H₂Ö: → Cl—COO⁻ N=C—O⁻ / O—H → Cl—COO⁻ N=C—O—H / O—H

Cl—COOH NH₂ ← dil. HCl ← Cl—COO⁻ NH₂ ← −CO₂ ← Cl—COO⁻ NH—C—O—H
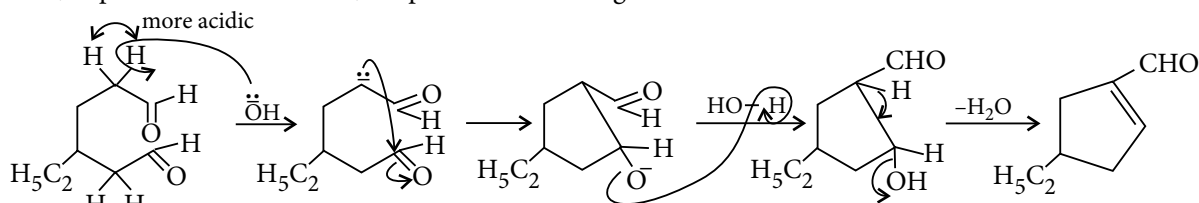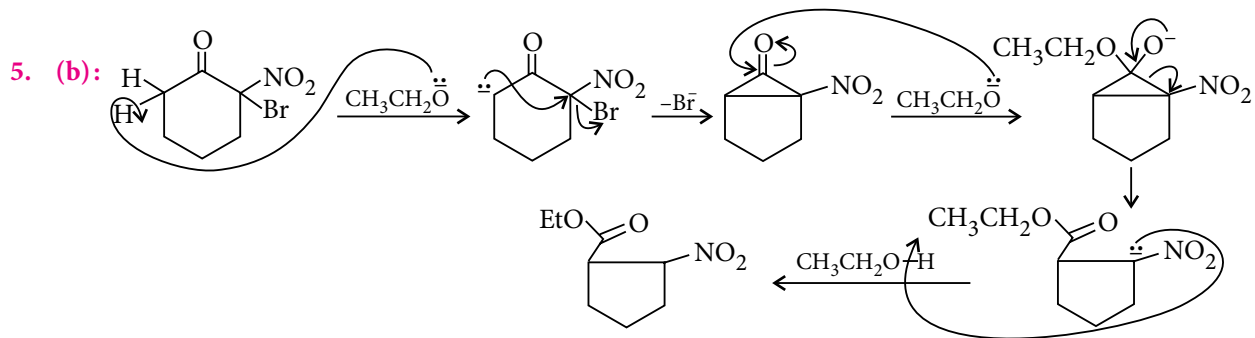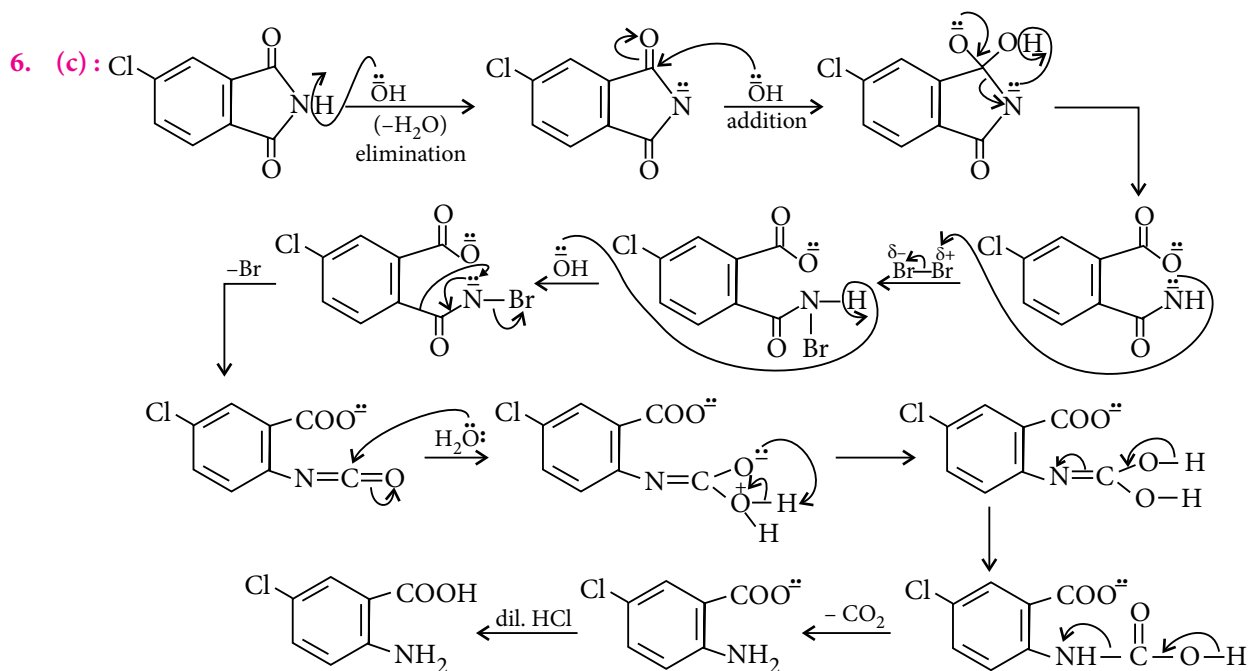
(–N̈H₂ group is not protonated as the lone pair very much participates in resonance with the benzene ring)

∴ Correct option is (c).

7. (a):

Me—C=N—ÖH → CF₃—C—O—C—CF₃ → Me—C=N⁺—O—C—CF₃ / O—C—CF₃ ... −CF₃COOH

→ Me—C=N⁺—O—C—CF₃

[Me—C⁺=N̈—◁ ↔ Me—C≡N⁺—◁] ← −CF₃COO⁻ (resonance stabilised)
(II)   (I)
(resonance stabilised)

(II) is more stable.

Me—$\overset{+}{\underset{}{C}}$=$\overset{..}{N}$—◁ $\xrightarrow{H_2\overset{..}{O:}}$ Me—C=N—◁ $\xrightarrow{-H^+}$ Me—C=$\overset{}{N}$—◁ $\xrightarrow{\text{tautomerisation}}$ Me—C—NH—◁
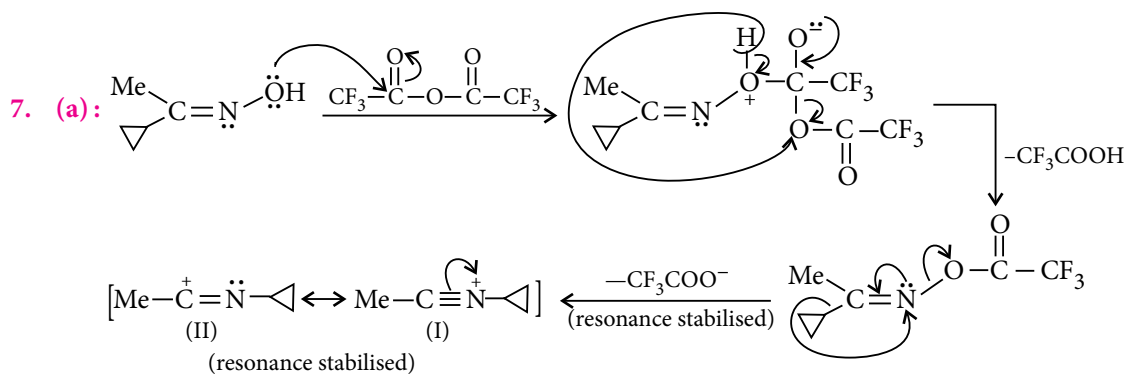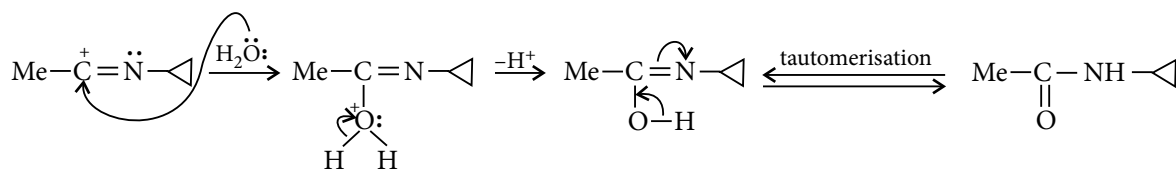
8. (d): (I) sp^3 hybridised, lone pair is involved in resonance.

(II) sp^3 hybridised, lone pair is involved very much in resonance and is more than (I).

(III) sp^3 hybridised, lone pair is involved in resonance

sp^2 hybridised, involvement of lone pair in resonance is not practical.

(IV) sp^3 hybridised, no question of participation of the lone pair in resonance and hence available for being protonated.

Now, in between (I) and (II), (I) is more basic, as in (II), participation of the lone pair in resonance is quite high.

In (III), one lone pair is very much available. So the order is : II < I < III < IV.

∴ Correct options is (d).

9. (d): ($NH_3 + H_2S$) converts —NO_2 into —NH_2. Rest part is quite common.

∴ Correct option is (d).

10. (a):

11. (c) :

(Electron donating group)
This makes the lone pair of nitrogen atom attached with the benzene ring directly, more available to react with the outer reagent without intervening into resonance.

∴ Correct option is (c).

CHEMISTRY MUSING

SOLUTION SET 45

1. (c) : Molecular mass of amine hydrochloride

$$= \frac{100}{\% \text{ of Cl}} \times \text{Atomic mass of Cl}$$

$$= \frac{100 \times 35.5}{32.42} = 109.5$$

∴ Molecular mass of amines (*A* to *G*)

  = molecular mass of amine hydrochloride
  – molecular mass of HCl

  = 109.5 – 36.5 = 73

Now, let the formula of amines (*A* to *G*) be $R\text{NH}_2$ or $C_n\text{H}_{2n+1}\text{NH}_2$

∴ $(12 \times n) + 1 \times (2n + 1) + 14 + 1 \times 2 = 73$

  $14n = 56 \implies n = 4$

∴ Molecular formula of amines = $C_4\text{H}_9\text{NH}_2$

2. (b) : According to Henderson's equation,

$$\text{pH} = \log \frac{[\text{salt}]}{[\text{acid}]} - \log K_a$$

$4 = \log [\text{salt}] - \log (0.1) - \log (1.8 \times 10^{-5})$

$\log [\text{salt}] = 4 - 1 - 5 + 0.2552 = -1.7448$

∴ $[\text{salt}] = 0.018 \text{ mol L}^{-1}$

Molecular weight of $CH_3COONa = 82 \text{ g mol}^{-1}$

Amount of salt = $0.018 \times 82 = 1.476 \text{ g L}^{-1}$

3. (b) : Given, $K_H = 1.67 \times 10^8 \text{ Pa}$

$P_{\text{CO}_2} = 2.5 \text{ atm} = 2.5 \times 101325 \text{ Pa}$

Applying Henry's law, $P_{\text{CO}_2} = K_H \times x_{\text{CO}_2}$

So, $x_{\text{CO}_2} = \dfrac{P_{\text{CO}_2}}{K_H} = \dfrac{2.5 \times 101325 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}} = 1.517 \times 10^{-3}$

Now, $x_{\text{CO}_2} = \dfrac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}} + n_{\text{CO}_2}} = \dfrac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}} = 1.517 \times 10^{-3}$ ...(i)

($\because n_{\text{CO}_2}$ is negligible)

For 500 mL of soda water,
volume of water = 500 mL; molar mass of water = 18 g

No. of moles of water, $n_{\text{H}_2\text{O}} = \dfrac{500}{18} = 27.78$

From eq. (i), we can write

$\dfrac{n_{\text{CO}_2}}{27.78} = 1.517 \times 10^{-3}$

∴ $n_{\text{CO}_2} = 42.14 \times 10^{-3}$

Mass of $\text{CO}_2 = 42.14 \times 10^{-3} \times 44 \text{ g} = 1.85 \text{ g}$

4. (b) : $CH_3CH_2CH_2CH_3 \xrightarrow[\text{Light}]{\text{Cl}_2, \, 298 \text{ K}}$

$\underset{\text{2-Chlorobutane}}{CH_3-\underset{\underset{\text{Cl}}{|}}{CH}-CH_2CH_3} + \underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl}$
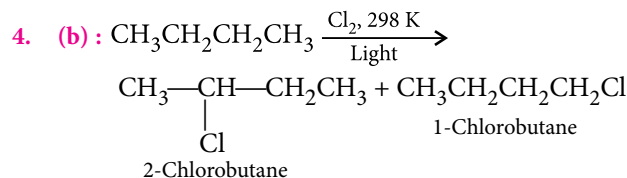
The relative rates of formation of these two isomeric chlorobutanes will be equal to (i) their number of types of H (1°, 2° or 3°) and (ii) their relative rates of substitution, *i.e.*,

$$\frac{\text{1-Chlorobutane}}{\text{2-Chlorobutane}}$$

$$= \frac{\text{No. of 1}° \text{ H}}{\text{No. of 2}° \text{ H}} \times \frac{\text{Reactivity of 1}° \text{ H}}{\text{Reactivity of 2}° \text{ H}}$$

$$= \frac{6}{4} \times \frac{1}{3.8} = \frac{6}{15.2}$$

Now, if *x* is the percentage of 1-chlorobutane, then percentage of 2-chlorobutane = 100 – *x*

∴ $\dfrac{x}{100 - x} = \dfrac{6}{15.2}$

On solving, we get *x* = 28%

Thus, percentage of 1-chlorobutane = 28%
and percentage of 2-chlorobutane = 72%

5. (a) : Velocity of electron in He⁺ ion in an orbit (*v*)

$$= \frac{2 \neq Ze^2}{nh}$$

Radius of He⁺ ion in an orbit $(r_n) = \dfrac{n^2 h^2}{4 \neq^2 m e^2 Z}$

∴ Angular frequency,

$$\omega = \frac{v}{r_n} = \frac{2\pi Z e^2 \times 4\pi^2 m e^2 Z}{nh \times n^2 h^2} = \frac{8\pi^3 Z^2 m e^4}{n^3 h^3}$$

$\because n = 2, m = 9.108 \times 10^{-28} \text{ g}, Z = 2,$
$h = 6.625 \times 10^{-27} \text{ erg sec}$
$e = 4.803 \times 10^{-10} \text{ esu}$

$$\omega = \frac{8 \times (22/7)^3 \times (2)^2 \times 9.108 \times 10^{-28} \times (4.803 \times 10^{-10})^4}{(2)^3 \times (6.625 \times 10^{-27})^3}$$

$= 2.067 \times 10^{16} \text{ sec}^{-1}$

6. (b) : $N_{Na_2S_2O_3} = M_{Na_2S_2O_3} \times$ no. of electrons lost by 1 molecule of $Na_2S_2O_3$ (*i.e.*, 1)

$$\because \quad 2S_2^{2+} \rightarrow S_4^{5/2+} + 2e^-$$
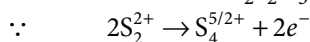
Meq. of I_2 formed = Meq. of $Na_2S_2O_3$ used

$$= 21.75 \times 0.0831 \times 1 = 1.807$$

$$\frac{w}{E} \times 1000 = 1.807 \quad \Rightarrow \quad \frac{w}{E} = \frac{1.807}{1000}$$

Also, $\dfrac{w}{E} = \dfrac{I.t}{96500}$

Thus, $\quad \dfrac{1.807}{1000} = \dfrac{I \times 2 \times 60 \times 60}{96500}$

$$I = 0.0242 \text{ A}$$

7. (c) :

$$3CH_3CH{=}CH_2 + BD_3 \xrightarrow{\text{THF}} \left(CH_3CH\underset{\underset{D}{|}}{-}CH_2\right)_3 B$$
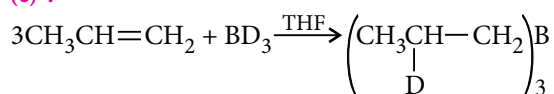
Trialkyl boranes reacts with organic acid, generally acetic acid, to give alkane corresponding to alkene.

$$\left(CH_3CH\underset{\underset{D}{|}}{-}CH_2\right)_3 B \xrightarrow{3CH_3COOH} 3CH_3{-}\underset{\underset{D}{|}}{CH}{-}\underset{\underset{H}{|}}{CH_2}$$

$$+ (CH_3COO)_3B$$

8. (c) :

$$3CH_3{-}CH{=}CH_2 \xrightarrow{BH_3/THF} \left(CH_3{-}\underset{\underset{H}{|}}{CH}{-}CH_2\right)_3 B$$

$$\xrightarrow{AgNO_3/NaOH} CH_3(CH_2)_4CH_3$$
$$(X)$$
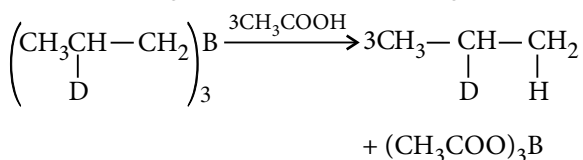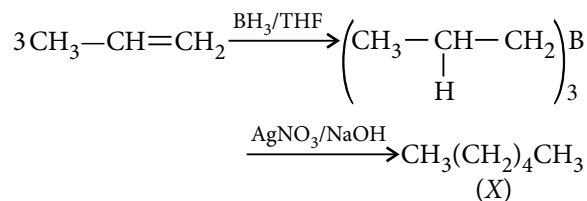
Trialkyl boranes undergo coupling reaction in presence of $AgNO_3$ / NaOH.

9. (4) : Phenol does not react with $NaHCO_3$ as it is less acidic in nature as compared to all others.

10. (2) :

S.No.	Colour of flame	Colour under uranium glass	Inference
1.	Golden yellow	Colourless	Sodium
2.	Violet	Deep red	Potassium
3.	Brick red	Yellow	Calcium
4.	Crimson red	Purple	Strontium
5.	Apple green	Bluish green	Barium
6.	Green with a blue centre	Bluish green	Copper

◈ ◈

JEE MAIN

SOLVED PAPER 2017

G☺☺D NEWS

We are happy to inform our readers that most of the questions asked in JEE Main 2017 Exam are very similar to the problems given in **MTG JEE Main Chemistry.**

G☺☺D NEWS

1. Given, $C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)}$;

$$\Delta_r H^° = -393.5 \text{ kJ mol}^{-1}$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}; \Delta_r H^°=-285.8 \text{ kJ mol}^{-1}$$

$$CO_{2(g)} + 2H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)};$$

$$\Delta_r H^° = +890.3 \text{ kJ mol}^{-1}$$

Based on the above thermochemical equations, the value of $\Delta_r H^°$ at 298 K for the reaction,

$C_{(graphite)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ will be
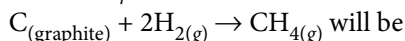
(a) $-74.8 \text{ kJ mol}^{-1}$ (b) $-144.0 \text{ kJ mol}^{-1}$

(c) $+74.8 \text{ kJ mol}^{-1}$ (d) $+144.0 \text{ kJ mol}^{-1}$

[*From MTG JEE Main Chemistry, Similar Question, Page 170, Illustration-5*]

2. 1 gram of a carbonate (M_2CO_3) on treatment with excess HCl produces 0.01186 mole of CO_2. The molar mass of M_2CO_3 in g mol^{-1} is

(a) 118.6   (b) 11.86

(c) 1186   (d) 84.3

3. ΔU is equal to

(a) adiabatic work   (b) isothermal work

(c) isochoric work   (d) isobaric work.

4. The Tyndall effect is observed only when following conditions are satisfied

(A) the diameter of the dispersed particle is much smaller than the wavelength of the light used

(B) the diameter of the dispersed particles is not much smaller than the wavelength of the light used

(C) the refractive indices of the dispersed phase and dispersion medium are almost similar in magnitude

(D) the refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

(a) (A) and (C)   (b) (B) and (C)

(c) (A) and (D)   (d) (B) and (D)

5. A metal crystallises in a face centred cubic structure. If the edge length of its unit cell is 'a', the closest approach between two atoms in metallic crystal will be

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

[*From MTG JEE Main Chemistry, Similar Question, Page 281, Q-70*]

6. Given:

$$E^°_{Cl_2/Cl^-} = 1.36 \text{ V}, \ E^°_{Cr^{3+}/Cr} = -0.74 \text{ V}$$

$$E^°_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33 \text{ V}, \ E^°_{MnO_4^-/Mn^{2+}} = 1.51 \text{ V}$$

Among the following, the strongest reducing agent is

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

[*From MTG JEE Main Chemistry, Similar Question, Page 350, Q-4*]

7. The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be (K_f for benzene = 5.12 K kg mol^{-1})
   (a) 74.6% (b) 94.6% (c) 64.6% (d) 80.4%
   [*From MTG JEE Main Chemistry, Similar Question, Page 322, Q-9*]

8. The radius of the second Bohr orbit for hydrogen atom is
   (Planck's constant (h) = 6.6262 × 10^{-34} J s;
   mass of electron = 9.1091 × 10^{-31} kg;
   charge of electron = 1.60210 × 10^{-19} C;
   permittivity of vacuum
   (ε_0) = 8.854185 × 10^{-12} kg^{-1} m^{-3} A^2)
   (a) 0.529 Å   (b) 2.12 Å
   (c) 1.65 Å   (d) 4.76 Å
   [*From MTG JEE Main Chemistry, Similar Question, Page 95, Q-22*]

9. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to
   (R = 8.314 J mol^{-1} K^{-1})
   (a) 6   (b) 4   (c) 8   (d) 12

10. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4 respectively. The pH of their salt (AB) solution is
    (a) 7.0   (b) 1.0   (c) 7.2   (d) 6.9
    [*From MTG JEE Main Chemistry, Similar Question, Page 260, Q-14*]

11. Both lithium and magnesium display several similar properties due to the diagonal relationship, however, the one which is incorrect, is
    (a) both form nitrides
    (b) nitrates of both Li and Mg yield NO_2 and O_2 on heating
    (c) both form basic carbonates
    (d) both form soluble bicarbonates.

12. Which of the following species is not paramagnetic?
    (a) O_2 (b) B_2 (c) NO   (d) CO
    [*From MTG JEE Main Chemistry, Similar Question, Page 152, Q-23*]

13. Which of the following reactions is an example of a redox reaction?
    (a) $XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

(b) $XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$
(c) $XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2$
(d) $XeF_2 + PF_5 \rightarrow [XeF]^+ PF_6^-$
   [*From MTG JEE Main Chemistry, Similar Question, Page 347, Q-4*]

14. A water sample has ppm level concentration of following anions, F$^-$ = 10; SO_4^{2-} = 100; NO_3^- = 50. The anion/anions that make/makes the water sample unsuitable for drinking is/are
    (a) only F$^-$ (b) only SO_4^{2-}
    (c) only NO_3^- (d) both SO_4^{2-} and NO_3^-

15. The group having isoelectronic species is
    (a) O^{2-}, F$^-$, Na, Mg^{2+}
    (b) O^-, F$^-$, Na$^+$, Mg^{2+}
    (c) O^{2-}, F$^-$, Na$^+$, Mg^{2+}
    (d) O^-, F$^-$, Na, Mg^{2+}
    [*From MTG JEE Main Chemistry, Similar Question, Page 159, Q-23*]

16. The products obtained when chlorine gas reacts with cold and dilute aqueous NaOH are
    (a) Cl$^-$ and ClO$^-$ (b) Cl$^-$ and ClO_2^-
    (c) ClO$^-$ and ClO_3^- (d) ClO_2^- and ClO_3^-
    [*From MTG JEE Main Chemistry, Similar Question, Page 679, Q-60*]

17. In the following reactions, ZnO is respectively acting as a/an
    (A) $ZnO + Na_2O \rightarrow Na_2ZnO_2$
    (B) $ZnO + CO_2 \rightarrow ZnCO_3$
    (a) acid and acid   (b) acid and base
    (c) base and acid   (d) base and base.
    [*From MTG JEE Main Chemistry, Similar Question, Page 710, Q-6*]

18. Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4. 'X' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. 'X' is
    (a) CH_3COONa (b) $Na_2C_2O_4$
    (c) C_6H_5COONa (d) HCOONa

19. The most abundant elements by mass in the body of a healthy human adult are : oxygen (61.4%), carbon (22.9%), hydrogen (10.0%) and nitrogen (2.6%). The weight which a 75 kg person would gain if all ^{1}H atoms are replaced by ^{2}H atoms is
    (a) 7.5 kg   (b) 10 kg
    (c) 15 kg   (d) 37.5 kg

20. On treatment of 100 mL of 0.1 M solution of $CoCl_3.6H_2O$ with excess $AgNO_3$, 1.2×10^{22} ions are precipitated. The complex is
(a) $[Co(H_2O)_6]Cl_3$
(b) $[Co(H_2O)_5Cl]Cl_2.H_2O$
(c) $[Co(H_2O)_4Cl_2]Cl.2H_2O$
(d) $[Co(H_2O)_3Cl_3].3H_2O$

[From MTG JEE Main Chemistry, Similar Question, Page 762, Q-19]

21. Which of the following compounds will form significant amount of *meta* product during mononitration reaction?

(a) NH₂

(b) NHCOCH₃

(c) OH

(d) OCOCH₃
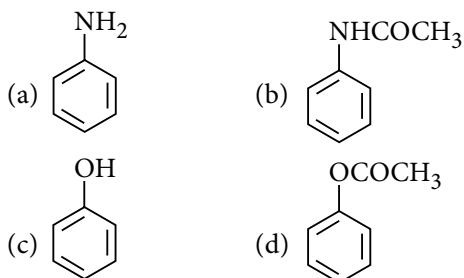
22. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine?

(a)

(b)

(c)

(d)
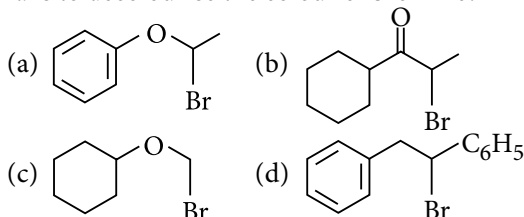
23. The formation of which of the following polymers involves hydrolysis reaction?
(a) Nylon 6, 6   (b) Terylene
(c) Nylon 6   (d) Bakelite

24. Which of the following molecules is least resonance stabilised?

(a)

(b)

(c)

(d)
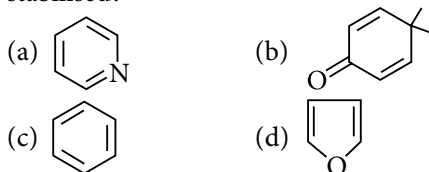
25. The increasing order of the reactivity of the following halides for the S_N1 reaction is

$$CH_3CHCH_2CH_3 \qquad CH_3CH_2CH_2Cl$$
$$|$$
$$Cl$$
(I)   (II)

$$p\text{-}H_3CO - C_6H_4 - CH_2Cl$$

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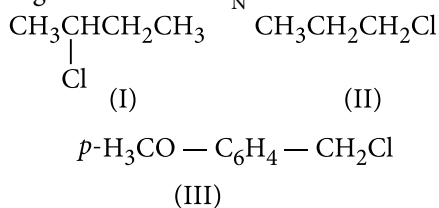
(a) (I) < (III) < (II)   (b) (II) < (III) < (I)
(c) (III) < (II) < (I)   (d) (II) < (I) < (III)

26. The major product obtained in the following reaction is

$$C_6H_5 \xrightarrow[\Delta]{t\text{-BuOK}}$$
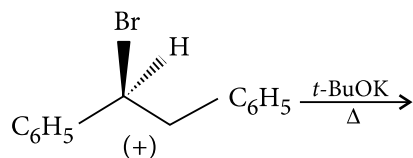
(a) $(+) - C_6H_5CH(Ot\text{-Bu})CH_2C_6H_5$
(b) $(-) - C_6H_5CH(Ot\text{-Bu})CH_2C_6H_5$
(c) $(\pm) - C_6H_5CH(Ot\text{-Bu})CH_2C_6H_5$
(d) $C_6H_5CH = CHC_6H_5$

27. Which of the following compounds will behave as a reducing sugar in an aqueous KOH solution?

(a)

(b)

(c)

(d)
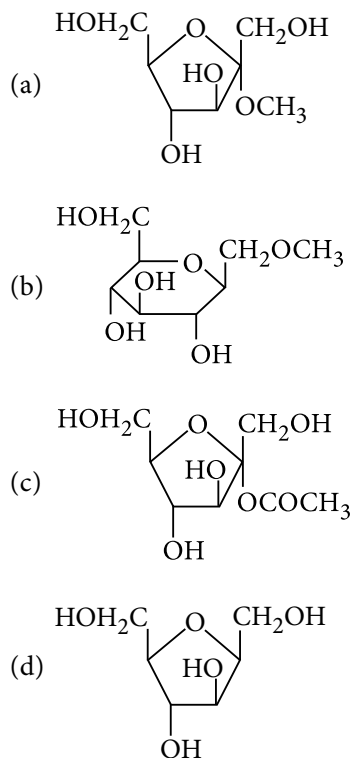
28. 3-Methylpent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is
(a) two   (b) four
(c) six   (d) zero.

29. The correct sequence of reagents for the following conversion will be

7. (b) : $\Delta T_f = 0.45°C$

w_2 (acetic acid) = 0.2 g

w_1 (benzene) = 20 g

$K_f = 5.12$ K kg mol^{-1}

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

$\therefore i = \dfrac{\Delta T_f}{K_f \times m} = \dfrac{0.45 \times 20 \times 60}{5.12 \times 0.2 \times 1000}$

$i = 0.527$

According to question,

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$
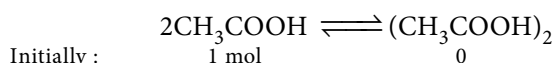
Initially :   1 mol   0

After time t : $(1 - \alpha)$ mol $\dfrac{\alpha}{2}$

$\Rightarrow i = 1 - \alpha + \dfrac{\alpha}{2}$

$i = 1 - \dfrac{\alpha}{2}$ ...(i)

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

$0.527 = 1 - \dfrac{\alpha}{2} \Rightarrow -0.946 = -\alpha$

$\alpha = 0.946$

$\therefore$ Percentage association of acetic acid in benzene

= 94.6%

8. (b) : Radius of nth orbit for H-atom is

$r = \dfrac{n^2 a_0}{Z} \text{Å}$

$r = \dfrac{(2)^2 \times 0.529}{1} \text{Å} \quad [\because n = 2, \text{ for second orbit}]$

$r = 2.12 \text{ Å}$

9. (b) : According to the Arrhenius equation,

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

For reaction R_1 ; $k_1 = Ae^{-E_{a_1}/RT}$

$\ln k_1 = \ln A - \dfrac{E_{a_1}}{RT}$

For reaction R_2 ; $k_2 = Ae^{-E_{a_2}/RT}$

$\ln k_2 = \ln A - \dfrac{E_{a_2}}{RT}$

Now, $\ln\left(\dfrac{k_2}{k_1}\right) = \dfrac{E_{a_1}}{RT} - \dfrac{E_{a_2}}{RT} = \dfrac{E_{a_1} - E_{a_2}}{RT} = \dfrac{\Delta E_a}{RT}$

$= \dfrac{10 \times 10^3 \text{ J mol}^{-1}}{8.314 \times 300} = 4$

10. (d) : pH of a salt of a weak acid and a weak base is given by :

$pH = 7 + \dfrac{1}{2}(pK_a - pK_b)$

$= 7 + \dfrac{1}{2}(3.2 - 3.4) = 6.9$

11. (c) : Due to diagonal relationship, both Li and Mg display some similar properties, but in the case of carbonates, Mg can form basic carbonates such as $3MgCO_3.Mg(OH)_2.3H_2O$. In contrast, Li only form typical carbonate Li_2CO_3 as other alkali metals. It does not form any basic carbonate having both carbonate and hydroxide ions.

12. (d) : (a) $O_2(16) : \sigma1s^2\ \sigma^*1s^2\ \sigma2s^2\ \sigma^*2s^2\ \sigma2p_z^2$
$\pi2p_x^2 = \pi2p_y^2,\ \pi^*2p_x^1 = \pi^*2p_y^1$

Number of unpaired electrons = 2 (paramagnetic)

(b) $B_2(10) : \sigma1s^2\ \sigma^*1s^2\ \sigma2s^2\ \sigma^*2s^2\ \pi2p_x^1 = \pi2p_y^1$

Number of unpaired electrons = 2 (paramagnetic)

(c) $NO(15) : \sigma1s^2\ \sigma^*1s^2\ \sigma2s^2\ \sigma^*2s^2\ \sigma2p_z^2$
$\pi2p_x^2 = \pi2p_y^2\ ^*2p_x^1$

Number of unpaired electron = 1 (paramagnetic)

(d) $CO(14) : \sigma1s^2\ \sigma^*1s^2\ \sigma2s^2\ \sigma^*2s^2\ \pi2p_x^2 = \pi2p_y^2$
$\sigma2p_z^2$

Number of unpaired electron = 0 (diamagnetic)

13. (c) : (a) $\overset{+6}{Xe}\overset{-1}{F_6} + \overset{+1}{H_2}\overset{-2}{O} \longrightarrow \overset{+6}{Xe}\overset{-2}{O}\overset{-1}{F_4} + 2\overset{+1}{H}\overset{-1}{F}$

No change in oxidation numbers, hence, no redox reaction occurs.

(b) $\overset{+6}{Xe}\overset{-1}{F_6} + 2\overset{+1}{H_2}\overset{-2}{O} \longrightarrow \overset{+6}{Xe}\overset{-2}{O_2}\overset{-1}{F_2} + 4\overset{+1}{H}\overset{-1}{F}$

No change in oxidation numbers hence, no redox reaction occurs.

(c)

decrease in O.No. (reduction)

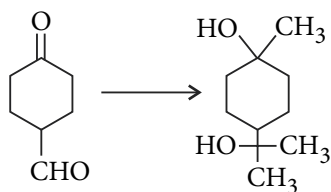$\overset{+4}{Xe}\overset{-1}{F_4} + \overset{+1}{O_2}\overset{-1}{F_2} \longrightarrow \overset{+6}{Xe}\overset{-1}{F_6} + \overset{0}{O_2}$

increase in O.No. (oxidation)
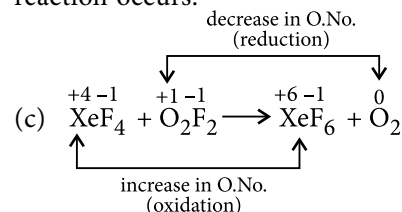
Hence, it is a redox reaction.

(d) $\overset{+2}{Xe}\overset{-1}{F_2} + \overset{+5}{P}\overset{-1}{F_5} \longrightarrow [\overset{+2}{Xe}\overset{-1}{F}]^+\ \overset{+5}{P}\overset{-1}{F_6}$

No change in oxidation numbers, hence, no redox reaction occurs.

14. (a) : Above 500 ppm of SO_4^{2-} ions in drinking water, can cause laxative effect otherwise lesser ppm value is permissible for drinking.

Maximum limit of NO_3^- ions in drinking water is 50 ppm, above this limit it can cause the disease like methemoglobinemia.

More than 1 ppm F^- ions in drinking water are not fit for drinking, it can cause decay of bones and teeth.

15. (c) : The species having same number of electrons are called isoelectronic species.
Number of e^-s in O^{2-} = 8 + 2 = 10
Number of e^-s in F^- = 9 + 1 = 10
Number of e^-s in Na^+ = 11 – 1 = 10
Number of e^-s in Mg^{2+} = 12 – 2 = 10
Therefore, the ions, given in option (c) are isoelectronic.

16. (a) : When Cl_2 gas reacts with cold and dilute aqueous NaOH, chloride (Cl^-) and hypochlorite (ClO^-) ions are formed.

$$Cl_2 + 2NaOH \xrightarrow{\text{Cold}} \underset{\substack{\text{(Sodium} \\ \text{chloride)}}}{NaCl} + \underset{\text{(Sodium hypochlorite)}}{NaOCl} + H_2O$$
$$\text{(dil.)}$$
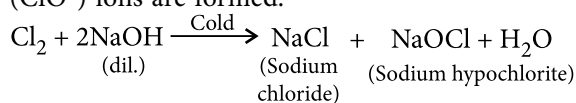
17. (b) : ZnO is an amphoteric oxide. So, it can act either as an acid or as a base.
In, $\underset{\text{acid}}{ZnO} + \underset{\text{base}}{Na_2O} \longrightarrow \underset{\text{salt}}{Na_2ZnO_2}$
ZnO acts as an acidic oxide.
In, $\underset{\text{base}}{ZnO} + \underset{\text{acid}}{CO_2} \longrightarrow \underset{\text{salt}}{ZnCO_3}$
ZnO acts as a basic oxide.
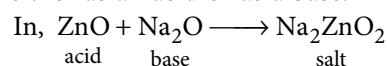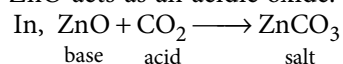
18. (b) : $\underset{(X)}{Na_2C_2O_4} + \underset{\text{(conc.)}}{H_2SO_4} \longrightarrow Na_2SO_4 + \underset{\text{(Oxalic acid)}}{H_2C_2O_4}$

$$H_2C_2O_4 \xrightarrow[-H_2O]{\text{conc. } H_2SO_4/\Delta} \underbrace{CO \uparrow + CO_2 \uparrow}_{\text{Effervescence}}$$

$$\underset{(X)}{Na_2C_2O_4} + CaCl_{2(aq)} \longrightarrow \underset{\text{(White ppt.)}}{CaC_2O_4 \downarrow} + 2NaCl$$

$$\underset{\text{(Purple)}}{5CaC_2O_4 \downarrow + 2KMnO_4 + 8H_2SO_4} \longrightarrow K_2SO_4$$
$$+ \underset{\text{(Colourless)}}{5CaSO_4 + 2MnSO_4 + 10CO_2 + 8H_2O}$$
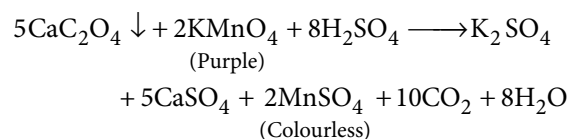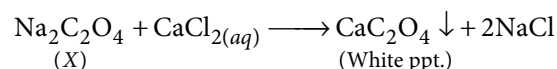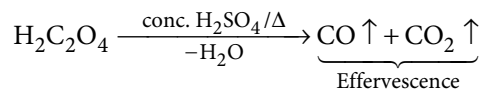
19. (a) : Mass of elements in the body of a healthy human adult are :
Oxygen (61.4%), carbon (22.9%), hydrogen (10%) and nitrogen (2.6%).
Weight of the person = 75 kg
Mass due to $^1H = 75 \times \dfrac{10}{100} = 7.5$ kg
On replacing ^1H by ^2H, 7.5 kg mass would replace with 15 kg.
$\therefore$ Net mass gained by person = (15 – 7.5) kg
$$= 7.5 \text{ kg}$$

20. (b) : Number of moles of complex
$$= \frac{M \times V(\text{mL})}{1000} = \frac{0.1 \times 100}{1000} = 0.01$$
Moles of ions precipitated with excess of $AgNO_3$
$$= \frac{1.2 \times 10^{22}}{6.022 \times 10^{23}} = 0.01992 \approx 0.02$$
Now, number of Cl^- ions present in ionisation sphere
$$= \frac{\text{Moles of ions precipitated with excess } AgNO_3}{\text{Moles of complex}}$$
$$= \frac{0.02}{0.01} = 2$$
Hence, the formula of complex is $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$.
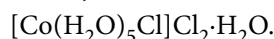
21. (a) : Conc. H_2SO_4 + conc. HNO_3 is a nitrating mixture. Aniline abstracts proton from sulphuric acid to give anilinium ion.
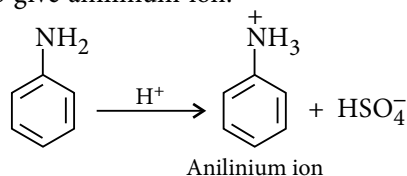
Due to electron withdrawing nature of anilinium ion, it acts as a *meta*-directing species in electrophilic aromatic substitution reactions.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

22. (c) :

(a)

(b)

(c) $\xrightarrow[S_N2]{tert\text{-BuONa}}$

(d) $\xrightarrow[E1]{tert\text{-BuONa}}$
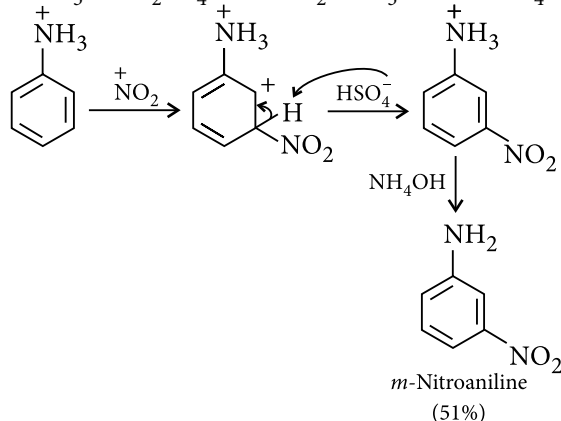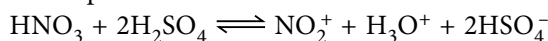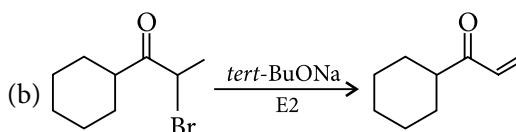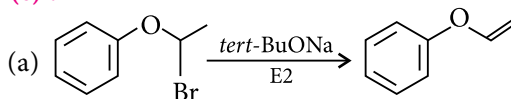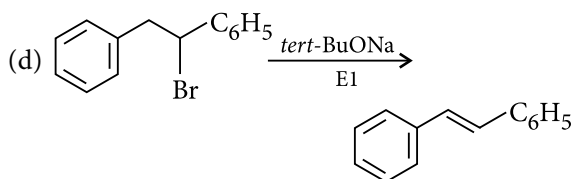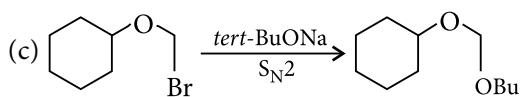
Due to absence of double or triple bond in the product formed in the reaction given in option (c), it does not decolourise bromine.

23. **(c) :** (a) Nylon 6, 6 is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and high temperature.

$$n\text{HOOC(CH}_2)_4\text{COOH} + n\text{H}_2\text{N(CH}_2)_6\text{NH}_2$$
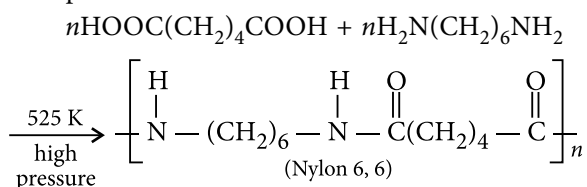
(b) Terylene is prepared by condensation polymerisation of ethylene glycol and terephthalic acid.

$$n[\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}]$$
Ethylene glycol
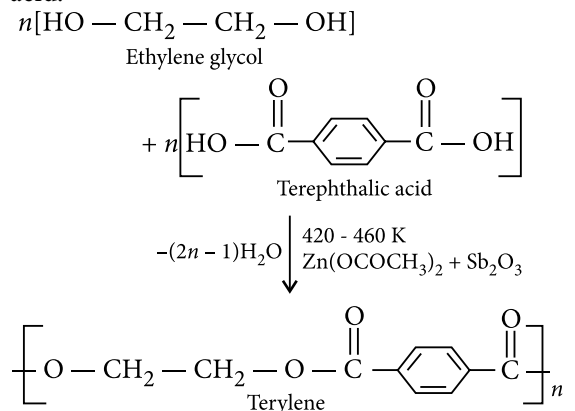
(c) Nylon 6 is prepared when caprolactam is hydrolysed to produce caproic acid which further undergoes condensation to produce nylon 6.
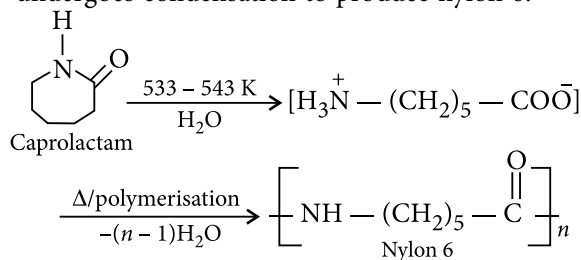
(d) Novolac on heating with formaldehyde undergoes cross-linkage to form bakelite.
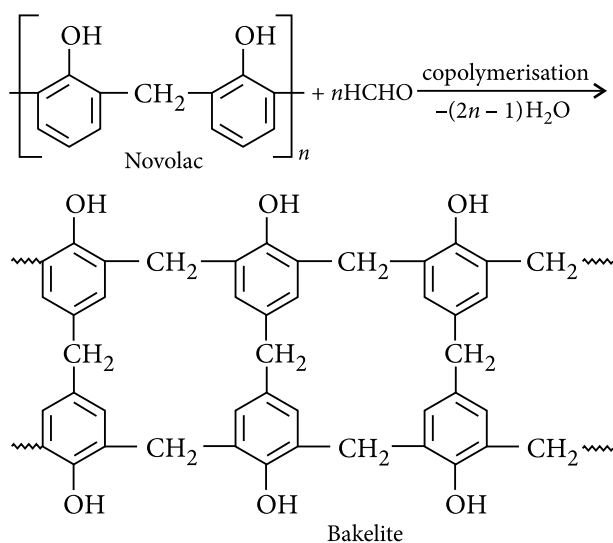
24. **(b) :**
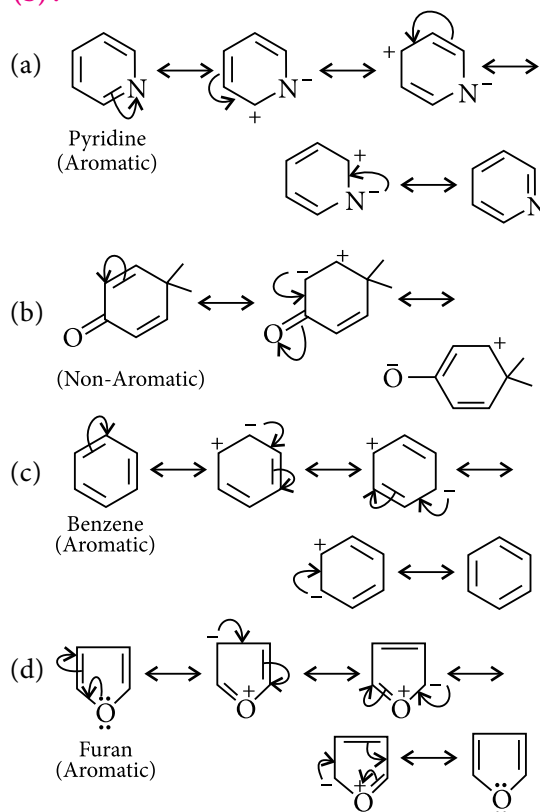
Greater the number of resonating structures, greater will be the stability of the compound. Aromatic compounds are resonance stabilised, hence, compound in option (b) is least resonance stabilised.

25. (d): More stable the carbocation formed, more rapidly that compound undergoes S_N1 reaction.

$$CH_3 — \underset{\underset{(I)}{\overset{|}{Cl}}}{CH} — CH_2 — CH_3 \xrightarrow{-Cl^-} CH_3 — \overset{+}{CH} — CH_2 — CH_3$$
2°-carbocation

$$CH_3 — CH_2 — CH_2 — Cl \xrightarrow[(II)]{-Cl^-} CH_3 — CH_2 — \overset{+}{CH_2}$$
1°-carbocation

benzyl carbocation
(Resonance stabilised)
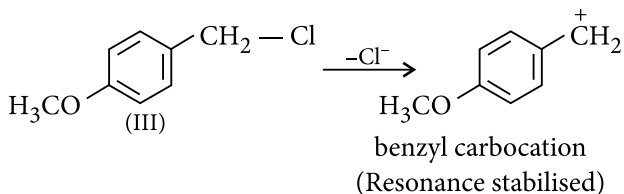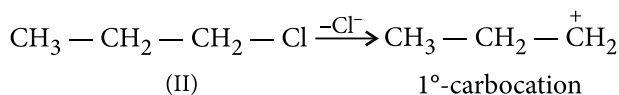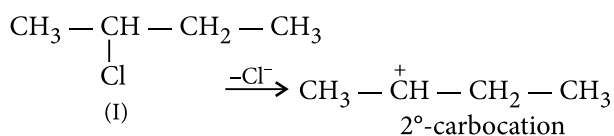
As, stability of carbocations,
benzyl carbocation > 2°–carbocation
> 1°–carbocation

Therefore, the reactivity of given compounds for the S_N1 reaction is : II < I < III

26. (d): *t*-BuOK is a bulky strong base and it undergoes dehydrohalogenation reaction more readily to form alkene. This reaction is proceed via E2–mechanism.

1, 2-Diphenylethene

$+$ *tert*-BuOH + KBr

27. (c):

(Free anomeric – OH group, reducing sugar)

28. (b):

$$\underset{\text{3-Methylpent-2-ene}}{CH_3 — CH_2 — \underset{\overset{|}{CH_3}}{C}=CH — CH_3} \xrightarrow[H_2O_2]{HBr}$$

$$CH_3 — CH_2 — \underset{\overset{|}{H}}{\overset{\overset{CH_3}{|}}{C^*}} — \underset{\overset{|}{Br}}{C^*H} — CH_3$$
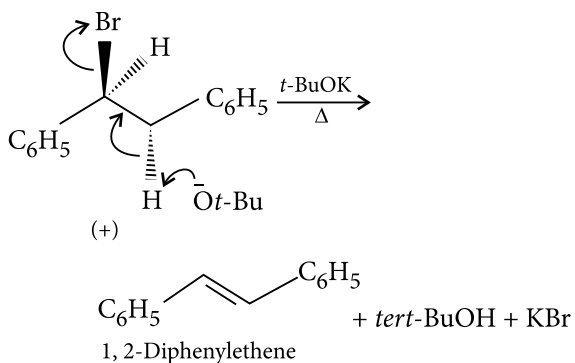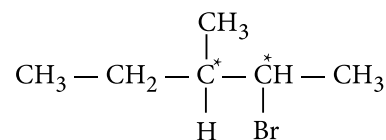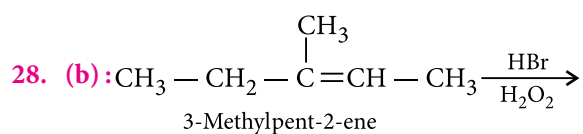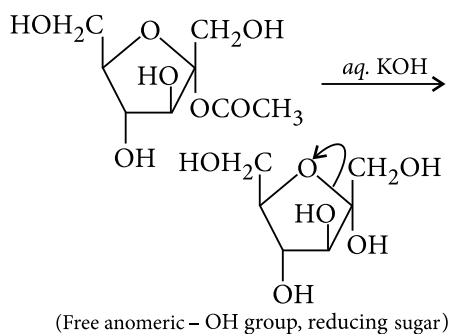
There are two chiral carbon atoms present in the product. Therefore, total number of stereoisomers are $= 2^n = 2^2 = 4$

29. (c):
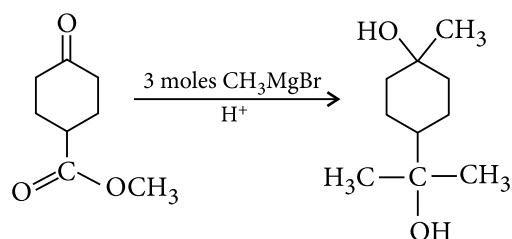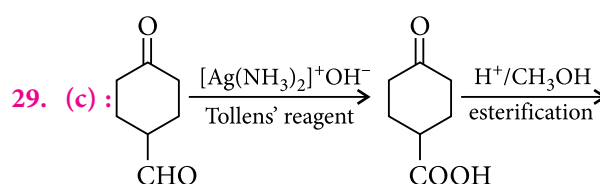
30. (d): DIBAL – H is a bulkier compound and a strong reducing agent which reduces cyanide, esters, lactone, amide, carboxylic acids into their corresponding aldehydes (partial reduction).

◈◈
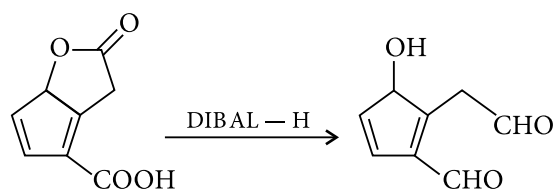
MPP-1 CLASS XII				ANSWER	KEY
1. (b)	**2.** (c)	**3.** (a)	**4.** (c)	**5.** (c)	
6. (a)	**7.** (d)	**8.** (b)	**9.** (d)	**10.** (a)	
11. (d)	**12.** (d)	**13.** (d)	**14.** (c)	**15.** (c)	
16. (d)	**17.** (a)	**18.** (c)	**19.** (b)	**20.** (a,b,c)	
21. (a,b)	**22.** (a,c)	**23.** (c,d)	**24.** (1)	**25.** (8)	
26. (4)	**27.** (a)	**28.** (c)	**29.** (d)	**30.** (b)	

CBSE BOARD
SOLVED PAPER
CLASS XII
2017

Time Allowed : 3 hours   Maximum Marks : 70

GENERAL INSTRUCTIONS

(i)   All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v)   Q. no. 23 is a value based question and carry 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

1. Write one similarity between physisorption and chemisorption.

2. Write the structure of 2,4-dinitrochlorobenzene.

3. For a reaction $R \longrightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?

4. Write the IUPAC name of the following compound:
   $CH_3NHCH(CH_3)_2$

5. Write the formula of an oxo-anion of chromium (Cr) in which it shows the oxidation state equal to its group number.

6. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.
   (Given : $\lambda°(H^+)$ = 349.68 S cm^{2}mol^{-1} and $\lambda°(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1})

7. Draw the structures of the following :
   (i) H_3PO_2 (ii) XeF_4

8. Define the following terms:
   (i) Ideal solution
   (ii) Molarity (M)

9. Complete the following reactions:
   (i) $Cl_2 + H_2O \longrightarrow$
   (ii) $XeF_6 + 3H_2O \longrightarrow$

OR

What happens when
(i) conc. H_2SO_4 is added to Cu?
(ii) SO_3 is passed through water?
Write the equations.

10. Write the reactions involved in the following:
    (i) Hell-Volhard-Zelinsky reaction
    (ii) Decarboxylation reaction

11. Write one difference in each of the following:
    (i) Lyophobic sol and lyophilic sol
    (ii) Solution and colloid
    (iii) Homogeneous catalysis and heterogeneous catalysis

12. Following compounds are given to you:
    2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane
    (i) Write the compound which is most reactive towards S_N2 reaction.
    (ii) Write the compound which is optically active.
    (iii) Write the compound which is most reactive towards β-elimination reaction.

13. Write the principles of the following methods:
    (i) Vapour phase refining
    (ii) Zone refining   (iii) Chromatography

14. A 10% solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water, if freezing point of pure water is 273.15 K.
(Given : Molar mass of sucrose = 342 g mol^{-1}, molar mass of glucose = 180 g mol^{-1})

15. Define the following :
(i) Cationic detergents
(ii) Narrow spectrum antibiotics
(iii) Disinfectants

16. (a) Calculate the mass of Ag deposited at cathode when a current of 2 ampere was passed through a solution of $AgNO_3$ for 15 minutes.
(Given : Molar mass of Ag = 108 g mol^{-1}, 1 F = 96500 C mol^{-1})
(b) Define fuel cell.

17. (i) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?
(ii) Why a solution of $[Ni(H_2O)_6]^{2+}$ is green while a solution of $[Ni(CN)_4]^{2-}$ is colourless?
(At. no. of Ni = 28)
(iii) Write the IUPAC name of the following complex : $[Co(NH_3)_5(CO_3)]Cl$.

18. Write the structures of compounds *A*, *B* and *C* in each of the following reactions :

(i) $C_6H_5Br \xrightarrow{\text{Mg/dry ether}} A \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } CO_{2(g)}} B \xrightarrow{PCl_5} C$

(ii) $CH_3CN \xrightarrow[\text{(b) } H_3O^+]{\text{(a) } SnCl_2/HCl} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\Delta} C$
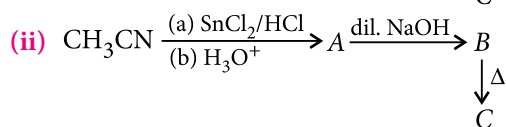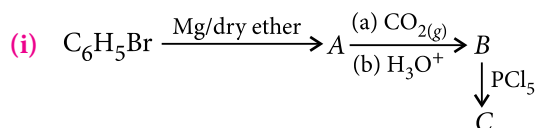
OR

Do the following conversions in not more than two steps:
(i) Benzoic acid to benzaldehyde
(ii) Ethyl benzene to benzoic acid
(iii) Propanone to propene

19. Write the structures of the monomers used for getting the following polymers:
(i) Neoprene
(ii) Melamine-formaldehyde polymer
(iii) Buna-S

20. Following data are obtained for the reaction :

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.
(b) Calculate the half-life.
(Given : log 2 = 0.3010, log 4 = 0.6021)

21. Give reasons :
(i) Acetylation of aniline reduces its activation effect.
(ii) CH_3NH_2 is more basic than $C_6H_5NH_2$.
(iii) Although —NH$_2$ is *o/p* directing group, yet aniline on nitration gives a significant amount of *m*-nitroaniline.

22. Give reasons:
(i) Thermal stability decreases from H_2O to H_2Te.
(ii) Fluoride ion has higher hydration enthalpy than chloride ion.
(iii) Nitrogen does not form pentahalide.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) potassium bromate and potassium iodate in bread and other bakery products, Ritu a class XII student decided to aware others about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct canteen contractor to stop selling sandwiches, pizza, burgers and other bakery products to the students. Principal took an immediate action and instructed the canteen contractor to replace the bakery products with some proteins and vitamins rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and students. After reading the above passage, answer the following questions :
(i) What are the values (at least two) displayed by Ritu?
(ii) Which polysaccharide component of carbo-hydrates is commonly present in bread?
(iii) Write the two types of secondary structure of proteins.
(iv) Give two examples of water soluble vitamins.

24. (a) Write the product(s) in the following reactions :

(i)

$$\xrightarrow[H^+]{(CH_3CO)_2O} ?$$

(ii) $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C}H - O - CH_2 - CH_3 \xrightarrow{HI} ? + ?$

(iii) $CH_3 - CH = CH - CH_2 - OH \xrightarrow{PCC} ?$
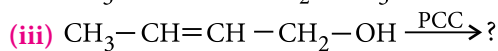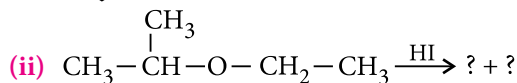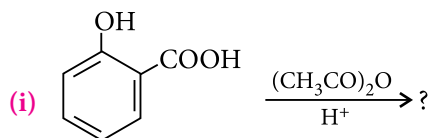
(b) Give simple chemical tests to distinguish between the following pairs of compounds :
  (i) Ethanol and phenol
  (ii) Propanol and 2-methylpropan-2-ol

OR

(a) Write the formula of reagents used in the following reactions :
  (i) Bromination of phenol to 2,4,6- tribromophenol
  (ii) Hydroboration of propene and then oxidation to propanol.

(b) Arrange the following compound groups in the increasing order of their property indicated :
  (i) *p*-nitrophenol, ethanol, phenol (acidic character)
  (ii) propanol, propane, propanal (boiling point)

(c) Write the mechanism (using curved arrow notation) of the following reaction :

$$CH_3 - CH_2 - \overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH}$$

$$CH_3 - CH_2 - \overset{\overset{\displaystyle +}{|}}{\underset{\underset{\displaystyle H}{|}}{O}} - CH_2 - CH_3 + H_2O$$
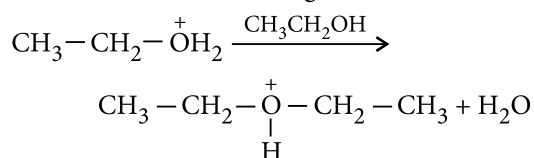
25. (a) Account the following :
  (i) Transition metals form large number of complex compounds.
  (ii) The lowest oxide of transition metal is basic whereas the highest oxide is amphoteric or acidic.
  (iii) $E°$ value for the Mn^{3+}/Mn^{2+} couple is highly positive (+1.57 V) as compare to Cr^{3+}/Cr^{2+}.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

OR

(a) (i) How is the variability in oxidation states of transition metals different from that of the *p*-block elements?

(ii) Out of Cu^+ and Cu^{2+}, which ion is unstable in aqueous solution and why?

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when treated with an alkali. Why?

(b) Chemistry of actinoids is complicated as compared to lanthanoids. Give two reasons.

26. (a) An element has atomic mass 93 g mol^{-1} and density 11.5 g cm^{-3}. If the edge length of its unit cell is 300 pm, identify the type of unit cell.

(b) Write any two differences between amorphous solids and crystalline solids.

OR

(a) Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a *fcc* structure. (Atomic mass of Al = 27 g mol^{-1})

(b) Give reasons :
  (i) In stoichiometric defects, NaCl exhibits Schottky defect and not Frenkel defect.
  (ii) Silicon on doping with phosphorus forms *n*-type semiconductor.
  (iii) Ferrimagnetic substances show better magnetism than antiferromagnetic substances.

SOLUTIONS

1. Physical adsorption and chemical adsorption both increase with increase in surface area of the adsorbent.

2.
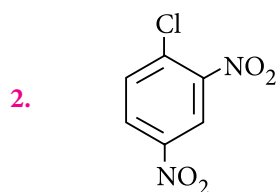
2, 4-Dinitrochlorobenzene

3. Half-life of first order reaction is independent of the initial concentration of reactants.

$$t_{1/2} = \frac{0.693}{k}$$

4. **Refer answer 1(iii), page no. 536**
(MTG Excel in Chemistry)

5. Oxo-anion of chromium in which it shows +6 oxidation state equal to its group number is $Cr_2O_7^{2-}$ (dichromate ion).

6. Degree of dissociation $(\alpha) = \dfrac{\Lambda_m}{\Lambda_m°}$

$$\alpha = \frac{39.05 \text{ S cm}^2 \text{mol}^{-1}}{(349.68 + 40.9) \text{ S cm}^2 \text{mol}^{-1}} = 0.1$$

7. **(i)** **Refer answer 65(i), page no. 290**
(*MTG Excel in Chemistry*)

(ii) **Refer answer 16(b), page no. 279**
(*MTG Excel in Chemistry*)

8. **(i)** **Refer answer 18, page no. 75**
(*MTG Excel in Chemistry*)

(ii) **Refer answer 32(ii), page no. 90**
(*MTG Excel in Chemistry*)

9. **(i)** $Cl_2 + H_2O \longrightarrow$ HCl + HOCl $\longrightarrow$
  Hydrochloric   Hypochlorous
    acid   acid

    2HCl + [O]
        Nascent
        oxygen
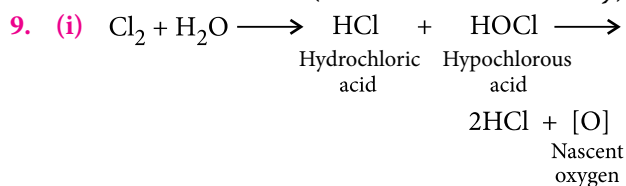
(ii) **Refer answer 23(i), page no. 275**
(*MTG Excel in Chemistry*)

OR

(i) When conc. H_2SO_4 reacts with Cu, CuO is formed which gets further converted into $CuSO_4$.

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$
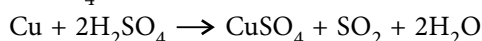
(ii) When SO_3 is passed through water, it dissolves SO_3 to give H_2SO_4.

$SO_3 + H_2O \longrightarrow H_2SO_4$
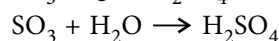
10. **(i)** **Refer answer 58, page no. 499**
(*MTG Excel in Chemistry*)

(ii) **Refer answer 16(iv), page no. 485**
(*MTG Excel in Chemistry*)

11. **(i)** **Refer answer 29, page no. 204**
(*MTG Excel in Chemistry*)

(ii) Solution : In true solution, the size of the particles is about 10^{-10} m.
Colloid : In a colloid, the size of the particles is between 10^{-7} to 10^{-9} m.

(iii) Homogeneous catalysis : Catalyst is present in the same phase as reactants.
Heterogeneous catalysis : Catalyst is present in a different phase as that of reactants.

12. **(i)** **Refer answer 55(i), page no. 415**
(*MTG Excel in Chemistry*)

(ii) 2-Bromopentane
(iii) 2-Bromo-2-methylbutane

13. **(i)** **Refer answer 26(iii), page no. 228**
(*MTG Excel in Chemistry*)

(ii) **Refer answer 4(i), page no. 224**
(*MTG Excel in Chemistry*)

(iii) Chromatography : Chromatographic method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent. The adsorbed components are removed using suitable eluent.

14. Molality (m) of sucrose solution

$$= \frac{w \times 1000}{M \times \text{Mass of solvent}} = \frac{10}{342} \times \frac{1000}{90}$$

$$= 0.325 \text{ m}$$

ΔT_f for sucrose solution $= T_f^\circ - T_f = (273.15 - 269.15)$ K

$$= 4 \text{ K}$$

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

$\therefore \quad K_f = \frac{\Delta T_f}{m} = \frac{4 \text{ K}}{0.325 \text{ m}} = 12.308 \text{ K/m}$

Molality of glucose solution $= \frac{10}{180} \times \frac{1000}{90}$

$$= 0.617 \text{ m}$$

$\Delta T_f = K_f \times m$

$\therefore \quad \Delta T_f = 12.308 \text{ K/m} \times 0.617 \text{ m}$

$$= 7.59 = 7.6 \text{ K}$$

$\therefore$ Freezing point of glucose solution, $T_f^\circ - \Delta T_f$

$$= (273.15 - 7.60) \text{ K} = 265.55 \text{ K}$$

15. **(i)** **Refer answer 21(ii), page no. 635**
(*MTG Excel in Chemistry*)

(ii) Narrow spectrum antibiotics : The antibiotics that are specifically effective against a limited group of microorganisms are known as narrow spectrum antibiotics.

(iii) Disinfectants : The chemical substances which kill microorganisms or stop their growth but harmful to human tissues are known as disinfectants.

16. **(a)** Given : $I = 2$ A, $t = 15$ min $= 15 \times 60$ s $= 900$ s
$w = ?$
$Q = I \times t = 2 \times 900 = 1800$ C
Reaction for deposition of Ag is as follows :

$Ag^+ + 1e^- \longrightarrow Ag$
  1 F   1 mol
1×96500 C   108 g
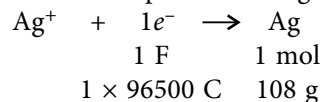
Thus, 1×96500 C of electricity is required to deposit 108 g of Ag.

$\therefore$ 1800 C of electricity would deposit

$$= \frac{108 \times 1800}{1 \times 96500} = 2.014 \text{ g of Ag}$$

(b) **Refer answer 55, page no. 126**
(*MTG Excel in Chemistry*)

17. (i) Refer answer 67(iii), page no. 378
(MTG Excel in Chemistry)
(ii) Refer answer 20, page no. 359
(MTG Excel in Chemistry)
(iii) Refer answer 18(b), page no. 370
(MTG Excel in Chemistry)

18. (i)

(ii)
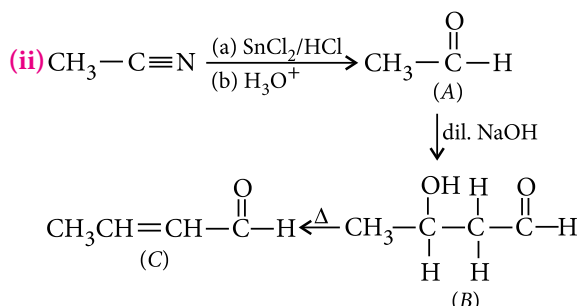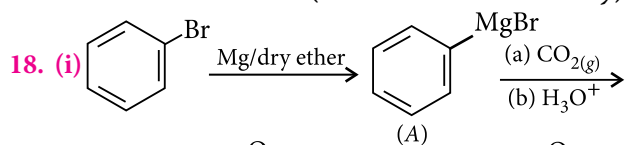
OR

(i) Refer answer 15(ii), page no. 484
(MTG Excel in Chemistry)
(ii) Refer answer 7(i), page no. 478
(MTG Excel in Chemistry)
(iii) Refer answer 15(i), page no. 484
(MTG Excel in Chemistry)

19. (i) Refer answer 17(iv), page no. 612
(MTG Excel in Chemistry)
(ii) Refer answer 18(ii), page no. 612
(MTG Excel in Chemistry)
(iii) Refer answer 17(i), page no. 611
(MTG Excel in Chemistry)

20. (a) The formula of rate constant for first order reaction is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

$$k_1 = \frac{2.303}{300 \text{ s}} \log \frac{(1.6 \times 10^{-2}) \text{ mol L}^{-1}}{(0.8 \times 10^{-2}) \text{ mol L}^{-1}} = 2.3 \times 10^{-3} \text{ s}^{-1}$$

Similarly, $k_2 = \frac{2.303}{600 \text{ s}} \log \frac{(1.6 \times 10^{-2}) \text{ mol L}^{-1}}{(0.4 \times 10^{-2}) \text{ mol L}^{-1}}$

$$= 2.3 \times 10^{-3} \text{ s}^{-1}$$

Unit and magnitude of rate constant shows the given reaction is of first order.

(b) The formula for half-life for first order reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.3 \times 10^{-3} \text{ s}^{-1}} = 301.30 \text{ s}$$

21. (i) After acetylation of aniline, acetanilide is formed in which due to the presence of

 group having $-I$ effect, electron density on N-atom decreases and hence, activation effect of aniline gets reduced.

(ii) Refer answer 70, page no. 552
(MTG Excel in Chemistry)
(iii) Refer answer 3(iv), page no. 537
(MTG Excel in Chemistry)

22. (i) As the size of central atom increases, $M-H$ bond becomes weaker and longer and hence, thermal stability decreases while going from H_2O to H_2Te.

(ii) As the size of halogen increases down the group from F to I, the hydration enthalpy of corresponding halide ion decreases. Hence F^- ion has higher hydration enthalpy (524 kJ mol^{-1}) than Cl$^-$ ion (378 kJ mol^{-1}).

(iii) Refer answer 16(ii), page no. 282
(MTG Excel in Chemistry)

23. (i) The two values displayed by Ritu are health consciousness and implementation of her knowledge for the welfare of others.

(ii) Starch is present in bread.

(iii) There are two types of secondary structure of proteins :
(a) α-helix
(b) β-pleated sheet structure

(iv) The two examples of water soluble vitamins are vitamin B complex and vitamin C.

24. (a) (i) Refer answer 27(ii), page no. 506
(MTG Excel in Chemistry)

(ii)
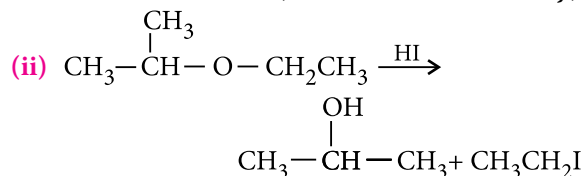
(iii) Refer answer 33, page no. 447
(MTG Excel in Chemistry)
(b) (i) Refer answer 29(i), page no. 458
(MTG Excel in Chemistry)

(ii) On oxidation in presence of acidic $KMnO_4$, 1° alcohol (propanol) will give aldehyde while 3° alcohol (2-methylpropan-2-ol) will give a ketone.

OR

(a) (i) Br_2/H_2O

(ii) BH_3 in THF/H_2O_2

(b) (i) *p*-nitrophenol > phenol > ethanol

(ii) Propanol > propanal > propane

(c) $CH_3-CH_2-\overset{+}{O}H_2 \quad \overset{CH_3-CH_2-\ddot{O}H}{\xrightarrow{S_N2 \text{ mechanism}}}$

$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_2-CH_3 + H_2O$
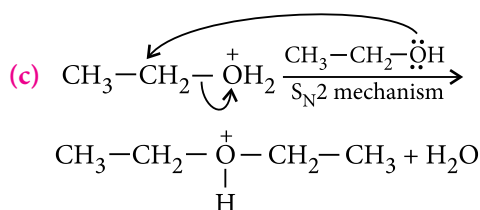
25. (a) (i) **Refer answer 16, page no. 324**
(*MTG Excel in Chemistry*)

(ii) As oxidation number of transition metals in their oxides increases, their acidic character increases due to lack of *d*-electrons. In the lowest oxide, oxidation state is lower and hence, it becomes basic and in highest oxide, oxidation state is higher and therefore, it becomes acidic or amphoteric.

(iii) **Refer answer 52(iv), page no. 335**
(*MTG Excel in Chemistry*)

(b) Similarity : The elements of both the series are electropositive in nature. They are reactive metals and act as strong reducing agents.
Difference : Lanthanoids except promethium are non-radioactive elements, while all actinoids are radioactive elements.

OR

(a) (i) **Refer answer 13, page no. 316**
(*MTG Excel in Chemistry*)

(ii) **Refer answer 9, page no. 314**
(*MTG Excel in Chemistry*)

(iii) Orange colour of $Cr_2O_7^{2-}$ ion changes to yellow when an alkali is added because on addition of an alkali, the concentration of H^+ ions decreases and hence, the reaction proceeds in the forward direction producing yellow solution containing CrO_4^{2-} ions.

$$\underset{\text{orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{yellow}}{2CrO_4^{2-}} + H_2O$$
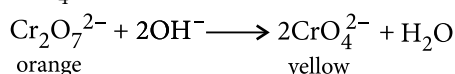
(b) Chemistry of actinoids is more complicated than lanthanoids because

(i) actinoids show greater number of oxidation states due to the comparable energies of 5*f*, 6*d* and 7*s* orbitals.

(ii) Most of the actinoids are radioactive and the study of their chemistry in the laboratory is difficult.

26. (a) Given, atomic mass (M) = 93 g mol^{-1},
density (d) = 11.5 g cm^{-3},
edge length (a) = 300 pm = 300×10^{-10} cm
$Z = ?$
We know that, $d = \dfrac{Z \times M}{N_A \times a^3}$

or, $Z = \dfrac{d \times N_A \times a^3}{M}$

$= \dfrac{11.5 \times 6.022 \times 10^{23} \times (3 \times 10^{-8})^3}{93} = 2.01 \approx 2$

So, type of the unit cell is *bcc*.

(b) **Refer answer 11, page no. 33**
(*MTG Excel in Chemistry*)

OR

(a) As 27 g of Al will contain 6.023×10^{23} atoms

$\therefore$ 8.1 g Al will contain $= \dfrac{6.023 \times 10^{23}}{27} \times 8.1$ atoms

$= 1.8069 \times 10^{23}$ atoms

In *fcc*, 4 atoms are present in one unit cell

$\therefore$ 1.8069×10^{23} atoms will be present in

$\dfrac{1.8069 \times 10^{23}}{4} = 4.517 \times 10^{22}$ unit cells.

(b) (i) Since Schottky defect is shown by highly ionic compounds having small difference in the size of cations and anions, whereas Frenkel defect is shown by compounds having large difference in the size of cations and anions. Therefore, NaCl exhibits Schottky defect.

(ii) Since group 15 elements (*e.g.*, phosphorus) have one electron excess to group 14 elements (*e.g.*, silicon) after forming four covalent bonds. Thus, the extra free electron is responsible for the formation of *n*-type semiconductor.

(iii) Ferrimagnetic substances have a net dipole moment due to unequal parallel and antiparallel alignment of magnetic moments whereas antiferromagnetic substances have net magnetic moment zero due to compensatory alignment of magnetic moments. Therefore, ferrimagnetic substances show better magnetism than antiferromagnetic substances.

◈ ◈

LEARN FAST

Some Important Halides of Group 13 and Group 14 Elements

TYPES OF HALIDES

○ **Ionic or salt-like halides :** Metals having relatively low ionisation energies, form halides which are ionic in nature. Some of the metals, in their lower oxidation states, also give essentially ionic halides. Due to high lattice energies, almost all the metallic fluorides are ionic substances.

  ◆ AlF_3 is essentially ionic, $AlCl_3$ dimer has intermediate character.

○ **Covalent or acidic halides :** These halides are given by non-metals, as well as by metals with high charge/size ratio. Examples are CCl_4, NF_3, PCl_3, etc.

○ **Complex halides :** The halides, whose central atom has vacant p-orbitals and/or vacant d-orbitals can accommodate lone pairs of electrons donated by the halide ions and can thus form complex halide ions. Examples are,
AlF_6^{3-}, $GaCl_4^-$, $TiBr_4^-$, SiF_6^{2-}, $SnCl_4^{2-}$, PCl_6^-, SbF_5^{2-}, etc.
F^- ion forms stable complex halide ions with smaller cations like B^{3+}, Al^{3+}, Si^{4+} because of strong electrostatic force and high energies of the resulting bonds.

HALIDES OF GROUP 13 ELEMENTS (BORON FAMILY)

○ All the elements of group-13 form trihalides (MX_3) (except TlI_3, which is not known) by direct combination with halogen.
$2M_{(s)} + 3X_{2(g)} \xrightarrow{\Delta} 2MX_3$ (X = F, Cl, Br or I)

○ All the trihalides of group 13 elements are known except Tl(III) iodide.

○ Due to small size and high electronegativity of boron, all boron halides are covalent in nature and act as Lewis acids. These halides exist as monomeric molecules having planar triangular geometry (sp^2 hybridisation).

○ All boron trihalides except BF_3, are hydrolysed to boric acid.
$BX_3 \cdot 3H_2O \longrightarrow B(OH)_3 + 3HX$;   ($X$ = Cl, Br, I)
However, BF_3 forms an addition product with water.
$BF_3 + H_2O \rightleftharpoons H^+[BF_3OH]^- \xrightarrow{H_2O} H_3O^+[BF_3OH]^-$

Being a Lewis acid and having less tendency for hydrolysis, BF_3 is used as a catalyst in organic reactions *e.g.*, Friedel–Crafts reaction.

○ Boron atom, in BX_3, has six electrons in the outermost orbit and thus, it can accept a pair of electrons from a donor molecule like NH_3 to complete its octet. Hence, boron halides act as very efficient Lewis acids.

Ammonia (electron donor)   Boron trifluoride (electron acceptor)

$$\text{or} \quad \left[H - N \rightarrow B - F \right]$$
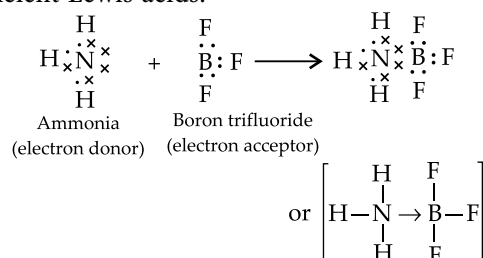
Similarly, $R_2O: + BF_3 \longrightarrow [R_2O \rightarrow BF_3]$

○ The relative Lewis acid characters of boron trihalides are found to obey the order :
$BI_3 > BBr_3 > BCl_3 > BF_3$

  ◆ This anomalous behaviour of BF_3 has been explained on the basis of the relative tendency of the halogen atom to back-donate its unutilised electrons to the vacant p-orbitals of boron atom. In boron trifluoride, each fluorine has completely filled unutilised $2p$-orbitals while boron has a vacant $2p$-orbital. Now since both of these orbitals belong to same energy level ($2p$), they can overlap effectively as a result of which fluorine electrons are transferred into the vacant $2p$-orbital of boron resulting in the formation of an additional $p\pi$-$p\pi$ bond. This type of bond formation is known as **back bonding** or **back donation**.

Completely filled $2p$-orbital of fluorine   Vacant $2p$-orbital of boron

Back bonding in BF_3 molecule
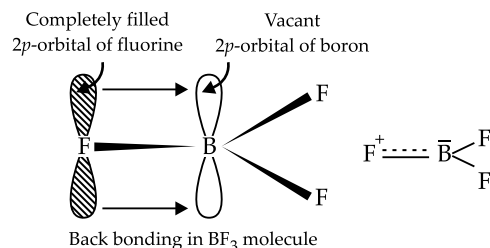
- ◆ Thus the B—F bond has some double bond character. Back bonding may take place between boron and any of the three fluorine atoms and thus boron trifluoride is regarded as a resonance hybrid of the following structures :

$$F^+ \text{---} \bar{B} {<}^F_F \longleftrightarrow F \text{---} \bar{B} {<}^{F^+}_F \longleftrightarrow F \text{---} \bar{B} {<}^F_{F^+}$$
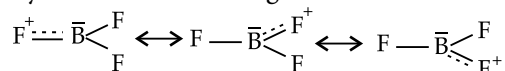
- ◆ As a result of back bonding, the electron deficiency of boron is reduced and hence Lewis acidic nature is decreased. The tendency for the formation of back bonding ($p\pi$-$p\pi$ bond) is maximum in BF_3 and decreases very rapidly from BF_3 to BI_3. Thus, BI_3, BBr_3 and BCl_3 are stronger Lewis acids than BF_3.

○ Lewis acid character of halides of the group 13 elements decreases in the order :

$$B > Al > Ga > In$$

○ Boron halides form complex halides of the type, $[BF_4^-]$, in which boron atom extends its coordination number to four by utilising empty p-orbital. It cannot extend its coordination number beyond four due to non-availability of d-orbitals. However, the other trihalides of this group form complex halides of the type $(AlF_6)^{3-}$, $(GaCl_6)^{3-}$ and $(InCl_6)^{3-}$ etc., where the central atom extends its coordination number to six by the use of d-orbitals.

○ The fluorides of Al, Ga, In and Tl are ionic and have high melting points.

○ Other halides of Al, Ga, In and Tl are largely covalent in anhydrous state and possess low melting points. These halides do not show backbonding because of increase in the size of the element. However, they make use of vacant p-orbitals by coordinate bond i.e., metal atoms complete their octet by forming dimers. Thus, aluminium chloride, aluminium bromide and indium iodide exist as dimers both in the vapour state and in the non-polar solvents.

Dimer structure of $AlCl_3$
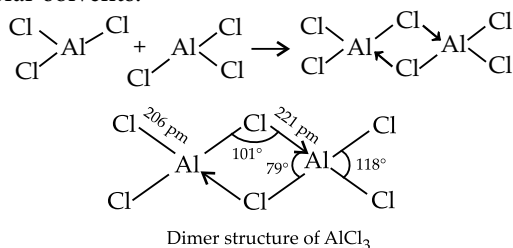
○ The dimer structure for Al_2Cl_6 is supported by the following facts :

- ◆ Vapour density of aluminium chloride measured at 400°C corresponds to the formula Al_2Cl_6.

- ◆ Bond distance between Al—Cl bond forming bridge is greater (2.21 Å) than the distance between Al—Cl bond present in the end (2.06 Å).

- ◆ The dimeric structure disappears when the halides are dissolved in water. This is due to high heat of hydration which splits the dimeric structure into $[M(H_2O)_6]^{3+}$ and X^- ions and the solution becomes good conductor of electricity.

$$Al_2Cl_6 + 12H_2O \longrightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$$

Therefore, Al_2Cl_6 is ionic in water.

○ In addition to trihalides, these elements form divalent as well as monovalent halides. Boron also forms B_2X_4 which is planar in solid state and non-eclipsed in liquid or vapour state.

(Planar structure)   (Non-eclipsed structure)
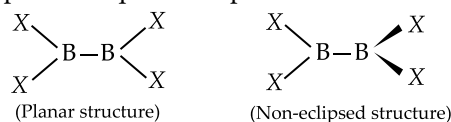
○ Monohalides (MX) are formed in gaseous state and they are very unstable halides. They are covalent in nature and covalent character decreases from B to Tl, and thallium halides are ionic in nature.

BORON HALIDES

○ Boron forms all the trihalides (BX_3), where X = F, Cl, Br or I.

Preparation

○ By direct combination : Under suitable conditions, boron reacts with halogens to form trihalides (BX_3).

$$2B + 3X_2 \longrightarrow 2BX_3$$

○ BF_3, an industrial catalyst may be prepared as follows :

$$3CaF_2 + B_2O_3 + 3H_2SO_4 \longrightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

○ Other boron trihalides (except BF_3) are prepared by following reaction :

$$B_2O_3 + 3C + 3X_2 \longrightarrow 2BX_3 + 3CO \ (X_2 = Cl_2, Br_2, I_2)$$

Properties

○ Due to small size of B^{3+}, these halides are covalent. They are non-electrolytes and do not conduct electricity in liquid state.

○ BF_3 is a colourless gas, BCl_3 is a colourless fuming liquid (b.pt. = 13°C), while BI_3 is a white fusible solid (m.pt. = 310°C).

○ Melting and boiling points of halides of boron (BX_3) decrease in the order :

$$BI_3 > BBr_3 > BCl_3 > BF_3$$

○ Boron halides (except BF_3) are readily hydrolysed in water.

○ Aqueous non-oxidising acids like HF, HCl and HI do not react even with colloidal boron but anhydrous HF reacts exothermically and forms BF_3.

ALUMINIUM TRIHALIDES

Preparation

○ AlF_3 is made by treating Al_2O_3 with HF gas at 700°C and the other trihalides are made by the direct exothermic combination of the elements.

Properties of crystalline AlX_3

○ AlF_3 differs from the other trihalides of Al in being non-volatile, insoluble, and in having a much greater heat of formation.

Property	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
m.pt./°C	1290	192.4	97.8	189.4
Sublimation pt. (1 atm)/°C	1272	180	256	382
ΔH_f°/kJ mol^{-1}	1498	707	527	310

$4AlCl_3 + 6POCl_3 \longrightarrow [Al(OPCl_3)_6]^{3+} + 3[AlCl_4]^-$

$2Al_2I_6 + 12POCl_3 \rightleftharpoons 4AlCl_3 + 12POCl_2I$

$AlCl_3 + 3LiY \longrightarrow 3LiCl + AlY_3$
$$(Y = R, NR_2, N = CR_2)$$

$AlCl_3 + 4LiY \longrightarrow 3LiCl + LiAlY_4$
$$(Y = R, NR_2, N = CR_2, H)$$
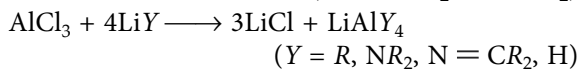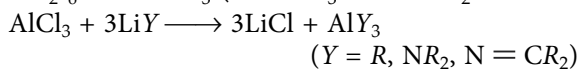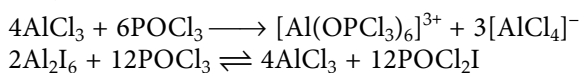
Similarly, $NaOR$ reacts to give $Al(OR)_3$ and $NaAl(OR)_4$. $AlCl_3$ also converts non-metal fluorides into the corresponding chlorides, *e.g.*,

$$BF_3 + AlCl_3 \longrightarrow AlF_3 + BCl_3$$

ALUMINIUM CHLORIDE, $AlCl_3$

Preparation

○ **Anhydrous aluminium chloride :** It is prepared by passing dry HCl gas or chlorine gas over heated aluminium turnings in the absence of air.

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$

$2Al + 3Cl_2 \longrightarrow 2AlCl_3$
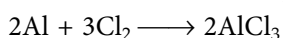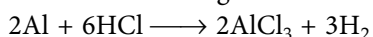
◆ A mixture of alumina and carbon on heating in a current of chlorine produces anhydrous $AlCl_3$.

$$Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000°C} 2AlCl_3 + 3CO$$
$$\text{Vapours}$$
$$\downarrow \text{cooled}$$
$$\text{Solid anhydrous}$$
$$\text{aluminium chloride}$$
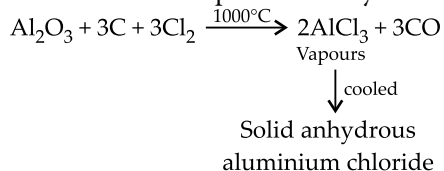
○ **Hydrated aluminium chloride :** $AlCl_3 \cdot 6H_2O$ is ionic and formed when aluminium metal or aluminium hydroxide is dissolved in dilute hydrochloric acid.

$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$

$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$
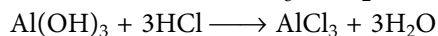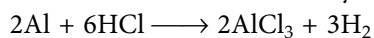
Chemical nature

○ Anhydrous aluminium chloride fumes in moist air due to the evolution of HCl.

$$Al_2Cl_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCl$$
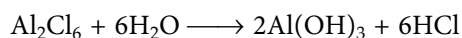
In water, it converts into hydrated aluminium chloride which is ionic in nature.

$$Al_2Cl_6 + 12H_2O \longrightarrow 2AlCl_3 \cdot 6H_2O$$
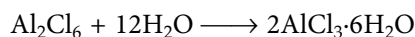
○ Anhydrous aluminium chloride forms an addition product with ammonia gas.

$$Al_2Cl_6 + 12NH_3 \longrightarrow 2[AlCl_3 \cdot 6NH_3]$$
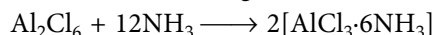
○ When ammonium hydroxide NH_4OH is added to the solution of aluminium chloride, a gelatinous precipitate of aluminium hydroxide appears which does not dissolve in excess of NH_4OH.

$$AlCl_3 + 3NH_4OH \longrightarrow \underset{\text{gelatinous ppt.}}{Al(OH)_3\downarrow} + 3NH_4Cl$$
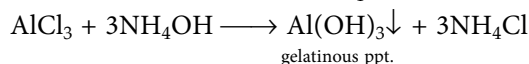
○ When sodium hydroxide (NaOH) is added to the solution of aluminium chloride drop by drop, a white gelatinous precipitate forms which dissolves in excess of sodium hydroxide forming sodium meta aluminate.

$$AlCl_3 + 3NaOH \longrightarrow \underset{\text{gelatinous ppt.}}{Al(OH)_3\downarrow} + 3NaCl$$

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$
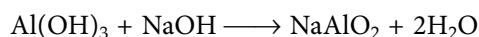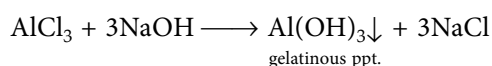
HALIDES OF GROUP 14 ELEMENTS (CARBON FAMILY)

○ Group-14 elements form covalent tetrahalides of the type MX_4 having tetrahedral nature, except $PbBr_4$ and PbI_4. The non-existence of $PbBr_4$ and PbI_4 is due to the fact that Pb^{4+} ion is a strong oxidising agent while Br^- and I^- ions are strongly reducing agents. Thus, Pb^{4+} ion cannot survive in presence of Br^- or I^- ion and is reduced to Pb^{2+} ion.

$Pb^{4+} + 2Br^- \longrightarrow Pb^{2+} + Br_2$
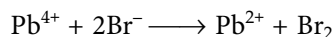
○ Except carbon, all other elements of group-14 also form dihalides such as MX_2. The stability of divalent halides increases down the group in accordance with inert pair effect.

○ The order of thermal stability of tetrahalides is :

$CX_4 > SiX_4 > GeX_4 > SnX_4 > PbX_4$

◆ The thermal stability and volatility of tetrahalides with a common central atom decreases with the increase in molecular weight of the tetrahalides *i.e.*,

$MF_4 > MCl_4 > MBr_4 > MI_4$

i.e., $CF_4 > CCl_4 > CBr_4 > CI_4$
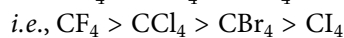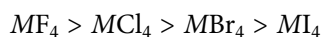
This is due to the decrease in the C — X bond energies from C — F to C — I.

- The tetrahalides (except carbon halides) are readily hydrolysed by water. The trend towards hydrolysis decreases down the group. Thus, silicon tetrachloride $SiCl_4$, fumes in moist air liberating hydrogen chloride.

$$SiCl_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid}}{Si(OH)_4} + 4HCl$$
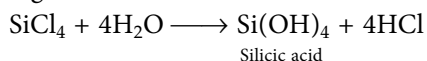
- Since carbon has no d-orbital, it cannot extend its coordination number beyond four, so its halides are not attacked (hydrolysed) by water. On the other hand, silicon and other elements of this group have vacant d-orbitals to which water molecules can coordinate and hence, their halides are hydrolysed by water.

- Due to the presence of vacant d-orbitals Si, Ge, Sn and Pb also form hexahaloanions of type $[MX_6]^{2-}$, in which atom is hexacoordinated (M = Si, Ge, Sn or Pb).

- The tetrahalides of carbon, on the other hand, do not form any complex ion because carbon has no d-orbital to accommodate any more electrons from the ligand (donor) like X^-.

HALIDES OF TIN

- **Stannous fluoride, SnF_2 :** It is obtained by reacting SnO with HF.

$$SnO + 2HF \longrightarrow SnF_2 + H_2O$$

- **Stannic fluoride, SnF_4 :** It can be prepared by gently heating $SnCl_4$ with excess of HF, until no more HCl is liberated.

$$SnCl_4 + 4HF \longrightarrow SnF_4 + 4HCl$$
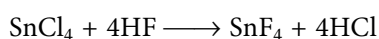
STANNOUS CHLORIDE, $SnCl_2$

Preparation

- Tin reacts with hot concentrated HCl to give hydrated $SnCl_2 \cdot 2H_2O$.

- Anhydrous $SnCl_2$ is formed when dry HCl gas is heated over tin or by heating a mixture of Sn and calculated quantity of mercuric chloride.

$$Sn + 2HCl_{(gas)} \longrightarrow SnCl_2 + H_2$$
$$Sn + HgCl_2 \longrightarrow SnCl_2 + Hg$$
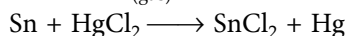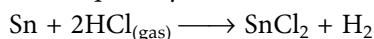
- Anhydrous salt cannot be obtained by heating the hydrated salts. On heating hydrolysis is noticed with the formation of a white solid (tin hydroxy chloride).

$$SnCl_2 \cdot 2H_2O \longrightarrow Sn(OH)Cl + H_2O + HCl$$
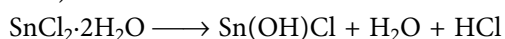
Physical properties

- It is a white crystalline solid, soluble in water, alcohol and ether.

- In water, it is hydrolysed readily. But, in presence of HCl, hydrolysis is reversed.

Chemical properties

- Reaction with alkalies : It reacts with NaOH, forms a white precipitate which dissolves in excess of alkali.

$$SnCl_2 + 2NaOH \longrightarrow \underset{\text{Stannous hydroxide}}{Sn(OH)_2} \downarrow + 2NaCl$$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + 2H_2O$$
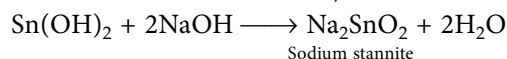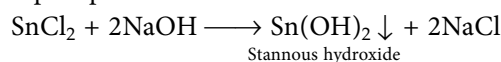
- Reaction with H_2S : It reacts with H_2S to give a dark brown ppt. of SnS. This precipitate is soluble in yellow ammonium sulphide, $(NH_4)_2S_2$, due to the formation of ammonium thiostannate $(NH_4)_2[SnS_3]$.

$$SnCl_2 + H_2S \longrightarrow \underset{\text{dark brown ppt.}}{SnS} \downarrow + 2HCl$$

$$SnS + \underset{\substack{\text{Yellow ammonium} \\ \text{sulphide}}}{(NH_4)_2S_2} \longrightarrow \underset{\substack{\text{Ammonium} \\ \text{thiostannate}}}{(NH_4)_2SnS_3}$$
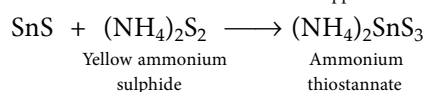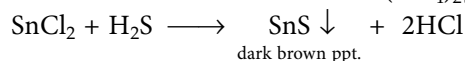
- Reducing properties : $SnCl_2$ acts as a strong reducing agent.
  - $SnCl_2$ reduces $HgCl_2$ to Hg_2Cl_2 (white ppt.) and finally to metallic Hg.
  $$2Hg^{2+} + Sn^{2+} \longrightarrow Hg_2^{2+} + Sn^{4+}$$
  $$Hg_2^{2+} + Sn^{2+} \longrightarrow 2Hg \downarrow + Sn^{4+}$$
  - It reduces ferric salts to ferrous salts and cupric salts to cuprous salts.
  $$2Fe^{3+} + Sn^{2+} \longrightarrow 2Fe^{2+} + Sn^{4+}$$
  $$2Cu^{2+} + Sn^{2+} \longrightarrow 2Cu^+ + Sn^{4+}$$
  - It reduces —NO_2 group is to —NH_2 group.
  $$3SnCl_2 + \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6HCl \longrightarrow$$
  $$3SnCl_4 + \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$
  - It decolourises iodine.
  $$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$
  - It reduces gold chloride to metallic gold sol (Purple of Cassius).
  $$3SnCl_2 + 2AuCl_3 \longrightarrow \underset{\text{Colloidal gold}}{2Au} + 3SnCl_4$$
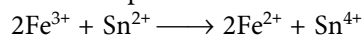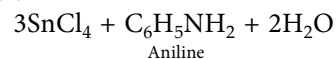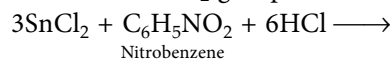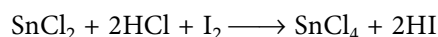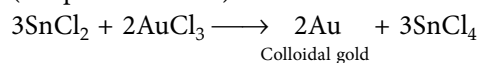
EXAM DATES 2017	
Karnataka CET	2nd May (Biology & Mathematics)
	3rd May (Physics & Chemistry)
NEET	7th May
MHT CET	11th May
COMEDK (Engg.)	14th May
BITSAT	16th May to 30th May (Online)
JEE Advanced	21st May
J & K CET	27th May to 28th May
AIIMS	28th May
JIPMER	4th June

STANNIC CHLORIDE, $SnCl_4$

○ $SnCl_4 \cdot 5H_2O$, is known as "butter of tin" or "oxymuriate of tin".

SnCl_4 is obtained by :

◆ Hydrolysis :

$$SnCl_4 + 4H_2O \longrightarrow \underset{\text{Stannic hydroxide}}{Sn(OH)_4} + 4HCl$$

◆ Reaction with conc. HCl :

$$SnCl_4 + 2HCl \longrightarrow \underset{\text{Chlorostannic acid}}{H_2SnCl_6}$$

◆ **Reaction with NH_4Cl :**

$$SnCl_4 + 2NH_4Cl \longrightarrow (NH_4)_2SnCl_6$$
Ammonium chlorostannate
(pink, used as mordant in
dyeing under the name pink salt)
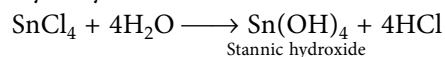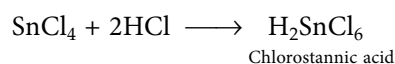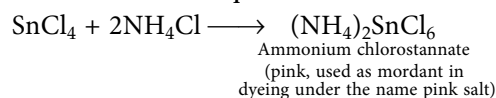
HALIDES OF LEAD

LEAD DIFLUORIDE, PbF_2

Preparation

○ It is formed :

◆ as a white ppt. when a soluble fluoride is added to a lead salt solution.

◆ by the action of HF on PbO or $Pb(CO_3)_2$.

Properties

○ It is a white powder with melting point 818°C.

LEAD TETRAFLUORIDE, PbF_4

Preparation

○ Passing F_2 over PbF_2 above 250°C.

$$PbF_2 + F_2 \xrightarrow{250°C} PbF_4$$

○ By dissolving red lead or freshly prepared PbO_2 in BrF_3.

$$3PbO_2 + 4BrF_3 \longrightarrow 3PbF_4 + 2Br_2 + 3O_2$$

LEAD CHLORIDE OR PLUMBOUS CHLORIDE, $PbCl_2$

Preparation

○ By adding HCl to aqueous solution of lead nitrate.

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2\downarrow + 2HNO_3$$

Properties

○ It is a white crystalline solid, slightly soluble in cold water but completely soluble in hot water.

○ It is fairly soluble in concentrated hydrochloric acid forming chloroplumbic acid.

$$PbCl_2 + 2HCl \longrightarrow H_2PbCl_4$$
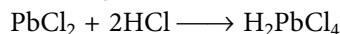
LEAD TETRACHLORIDE OR PLUMBIC CHLORIDE, $PbCl_4$

Preparation

○ It is prepared by dissolving lead dioxide in a well-cooled hydrochloric acid.

$$PbO_2 + 4HCl \rightleftharpoons PbCl_4 + 2H_2O$$
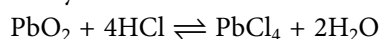
Properties

○ It is only slightly stable.

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

○ It is decomposed by excess of water.

○ It forms a double chloride with ammonium chloride known as ammoniumplumbichloride or ammoniumchloroplumbate, $(NH_4)_2PbCl_6$. Although the later compound is fairly stable, when treated with sulphuric acid it decomposes back to lead tetrachloride.

$$[(NH_4)_2PbCl_6] + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + PbCl_4 + 2HCl$$
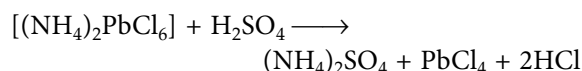
LEAD DIIODIDE, PbI_2

○ It is formed :

◆ by dissolving lead, its oxide or carbonate in HI.

◆ by adding a soluble iodide to a lead salt solution. It forms golden-yellow crystals with melting point 402°C and boiling point 872°C. On heating it first turns brick red and then brown red but regains its original colour on cooling. It dissolves in a large excess of KI forming $K[PbI_3]$ which is decomposed on dilution with water depositing PbI_2 again.

◈ ◈

MPP-1 | MONTHLY Practice Problems

Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

The Solid State | Solutions

Total Marks : 120

Time Taken : 60 Min.

NEET / AIIMS
Only One Option Correct Type

1. A metal crystallises in face-centred cubic lattice with edge length of 450 pm. Molar mass of metal is $50\,g\,mol^{-1}$. The density of the metal is
   (a) $3.12\,g\,cm^{-3}$
   (b) $3.64\,g\,cm^{-3}$
   (c) $3.95\,g\,cm^{-3}$
   (d) $4.02\,g\,cm^{-3}$

2. The osmotic pressure of a urea solution is 500 mm Hg at 10 °C. The solution is diluted and its temperature is raised to 25 °C. It is now found that osmotic pressure of the solution is reduced to 105.3 mm Hg. The extent of dilution of the solution is
   (a) 3 times (b) 4 times (c) 5 times (d) 6 times.

3. KCl crystallises in the same type of lattice as does NaCl. Given that, $r_{Na^+}/r_{Cl^-} = 0.55$ and $r_{K^+}/r_{Cl^-} = 0.74$. Calculate the ratio of the side of the unit cell of KCl to that of NaCl.
   (a) 1.123   (b) 0.891   (c) 1.414   (d) 0.414

4. A 0.025 M solution of monobasic acid has a freezing point of – 0.060 °C. The pK_a for the acid is
   (a) 1.2   (b) 2   (c) 2.5   (d) 5.7

5. A face centred cubic lattice of a single type of atoms has same defects and its one corner and one face centre is left unoccupied per unit cell. Calculate the packing fraction of such solid.
   (a) 0.325   (b) 0.256   (c) 0.625   (d) 0.312

6. Relative decrease in vapour pressure of an aqueous solution containing 2 moles of $[Cu(NH_3)_3Cl]Cl$ in 3 moles of H_2O is 0.50. On reaction with $AgNO_3$, this solution will form

   (a) 1 mol AgCl
   (b) 0.25 mol AgCl
   (c) 2 mol AgCl
   (d) 0.40 mol AgCl.

7. In a close packed structure of mixed oxides, it is found that lattice has O^{2-} (oxide ions), and one-half of octahedral voids are occupied by trivalent cations (A^{3+}) and one-eighth of tetrahedral voids are occupied by divalent cations (B^{2+}). What will be the formula of the mixed oxide?
   (a) $A_{1/6}B_{1/4}O$
   (b) $A_{1/2}B_{1/6}O$
   (c) $A_3B_2O_4$
   (d) A_2BO_4

8. The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what will be the partial pressure of the gas?
   (a) 0.625 bar
   (b) 0.762 bar
   (c) 0.529 bar
   (d) 0.232 bar

9. Which one of the following statements is incorrect?
   (a) The conductivity of metals decreases with increase in temperature.
   (b) The conductivity of semiconductors increases with increase in temperature.
   (c) There is no superconductor at room temperature.
   (d) Ionic solids conduct electricity due to presence of ions.

10. An element X of atomic mass 25.0 exists as X_4 in benzene to the extent of 100%. When 10.30 g of saturated solution of X in benzene is added to 20.0 g of benzene, the depression in freezing point of the resulting solution is 0.51 K. If K_f for benzene is 5.1 K kg mol^{-1}, the solubility of X in 100 g of benzene will be
   (a) 3.0 g   (b) 2.7 g   (c) 0.30 g   (d) 0.27 g

11. Tungsten has a body centred cubic lattice, and each lattice point is occupied by one atom. What will be the metallic radius of the tungsten atom, if the density of tungsten is 19.30 g cm^{-3} and atomic weight is 183.9 g?
(a) 2.129 Å
(b) 6.253 Å
(c) 3.163 Å
(d) 1.369 Å

12. Dry air contains 79% N_2 and 21% O_2. Determine the proportion of N_2 and O_2 (in terms of mole fractions) dissolved in water at 1 atm pressure. Henry's law constant for N_2 and O_2 in H_2O are 8.54×10^4 atm and 4.56×10^4 atm respectively.
(a) 1 : 2   (b) 3 : 1   (c) 1 : 3   (d) 2 : 1

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** Due to Frenkel defect, density of the crystalline solid decreases.
Reason : In Frenkel defect, cation or anion leaves the crystal.

14. **Assertion :** Out of the various colligative properties, osmotic pressure is used for the determination of molecular masses of polymers.
Reason : Polymer solutions do not possess a constant boiling point or freezing point.

15. **Assertion :** The number of tetrahedral voids is double the number of octahedral voids.
Reason : The size of the tetrahedral void is half of that of the octahedral void.

JEE MAIN / JEE ADVANCED / PETs
Only One Option Correct Type

16. A mixture of chlorobenzene and water (which are virtually immiscible) boils at 90.3°C at an external pressure of 740.2 mm. The vapour pressure of pure water at 40.3°C is 530.1 mm. What is the percent weight of chlorobenzene in the distillate?
(a) 20.21   (b) 37.19   (c) 28.74   (d) 71.26

17. If an element (at. wt. = 50 u) crystallises in *fcc* lattice, with edge length, a = 0.5 nm. What is the density of unit cell, if it contains 4% Schottky defects? ($N_A = 6.023 \times 10^{23}$)

(a) 2.55 g/cc
(b) 2.66 g/cc
(c) 2.26 g/cc
(d) 1.0 g/cc

18. A solution of A and B with 30 mole percent of A is in equilibrium with its vapour which contains 60 mole percent of A. Assuming that the solution and the vapour behave ideally, the ratio of the vapour pressures of pure A and pure B is
(a) 1.5   (b) 2.5   (c) 3.5   (d) 4.5

19. The number of C-atoms present in the unit cell of diamond and the packing efficiency respectively are
(a) 6, 50.24%
(b) 8, 34%
(c) 8, 74%
(d) 6, 68%

More than One Options Correct Type

20. The total vapour pressure of a binary solution ($n_A = n_B$) is given by $p = (110x_A + 125x_B)$ mm Hg, where x_A and x_B are the mole fractions of components A and B, respectively. It suggests that
(a) the vapour pressure of solution is less than the pure component B
(b) the vapour pressure of solution is more than that of pure component A
(c) vapour pressure of pure component A is 110 mm Hg and that of pure component B is 125 mm Hg
(d) the vapour pressures of pure components A and B are 125 mm Hg and 110 mm Hg, respectively.

21. Choose the correct statements out of the following.
(a) Quartz is a three-dimensional silicate.
(b) There is no effect on density of a solid having Frenkel defect.
(c) Group-14 elements doped with Group-13 elements produce *n*-type semiconductors.
(d) Ferrimagnetic substances possess large magnetic moments.

22. Which of the following statements are correct about Henry's constant, K_H?
(a) Greater the value of K_H, lower is the solubility of the gas at the same pressure and temperature.
(b) K_H decreases with increase in temperature.
(c) The unit of K_H is kbar.
(d) All noble gases have the same value of K_H at the same temperature.

23. The melting point of RbBr is 682 °C, while that of NaF is 988 °C. What is the principal reason that melting point of NaF is much higher than that of RbBr?

(a) The two crystals are not isomorphous.

(b) The molar mass of NaF is smaller than that of RbBr.

(c) The intermolecular distance $(r_c + r_a)$ is greater for RbBr than that for NaF.

(d) The bond in RbBr has less covalent character than the bond in NaF.

Integer Answer Type

24. The mole fraction of $CCl_{4(g)}$ when its vapours is in equilibrium with the liquid mixture of CCl_4 and $SiCl_4$ is 0.3474. The vapour pressures of $SiCl_4$ and CCl_4 are 238.3 and 114.9 mm Hg respectively at the same temperature. Weight ratio of CCl_4 and $SiCl_4$ is $x/1$. The value of x is

25. The coordinaton number of the cation in an ionic compound A^+B^- in which the radius of A^+ is 148 pm and that of B^- is 195 pm is

26. A mixture of H_2O and $C_6H_5NO_2$ boils at 99°C. In the vapours of mixture, partial vapour pressures of H_2O and $C_6H_5NO_2$ are 733 mm Hg and 27 mm Hg respectively. The ratio $w_{H_2O}/w_{C_6H_5NO_2}$ is

Comprehension Type

A spinel is a class of oxides in which two types of cations are present, bivalent cations and trivalent cations. Oxide ions are arranged in *ccp* layers, bivalent cations occupy $1/8^{th}$ of the tetrahedral voids. Trivalent cations occupy half of the total number of octahedral voids.

27. If A is a bivalent and B is a trivalent cation, what is formula of oxide having spinel structure?

(a) AB_2O_4 (b) A_2BO_4

(c) ABO_8 (d) $A_3B_2O_6$

28. If $\dfrac{r_+}{r_-}$ lies between 0.414 to 0.732, the cation will occupy

(a) trigonal void   (b) tetrahedral void

(c) octahedral void   (d) cubic void.

Matrix Match Type

29. Match the Column I with Column II and mark the appropriate option.

Column I	Column II
(A) Osmotic pressure	(P) Directly proportional to van't Hoff factor, i (in the same solvent)
(B) Vapour pressure	(Q) Inversely proportional to van't Hoff factor, i (in the same solvent)
(C) Freezing point	(R) Directly proportional to molecular mass of the solute (in the same solvent)
(D) Boiling point	(S) Directly proportional to molecular mass of the solvent (for the same solute)

	A	B	C	D
(a)	P, S	Q, R	P	Q, R
(b)	R, S	P, Q	R, S	P
(c)	Q	P	P, R	Q, S
(d)	P	Q, R	Q, R	P, S

30. Match the Column I with Column II and mark the appropriate option.

Column I	Column II
(A) Cubic	(P) Face-centred
(B) Tetragonal	(Q) Body-centred
(C) Orthorhombic	(R) $a \neq b \neq c$
(D) Monoclinic	(S) $\alpha = \beta = \gamma = 90°$

	A	B	C	D
(a)	P, Q	P, Q, S	R	S
(b)	P, Q, S	Q, S	P, Q, R, S	R
(c)	R	Q	P, R	Q, S
(d)	P, S	Q, S	P, Q, R	Q

◈ ◈

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SELF CHECK ✎

Check your score! If your score is

No. of questions attempted	......	> 90%	EXCELLENT WORK ! You are well prepared to take the challenge of final exam.
No. of questions correct	......	90-75%	GOOD WORK ! You can score good in the final exam.
Marks scored in percentage	......	74-60%	SATISFACTORY ! You need to score more next time.
		< 60%	NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

MPP-1 | MONTHLY Practice Problems

Class XI

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.
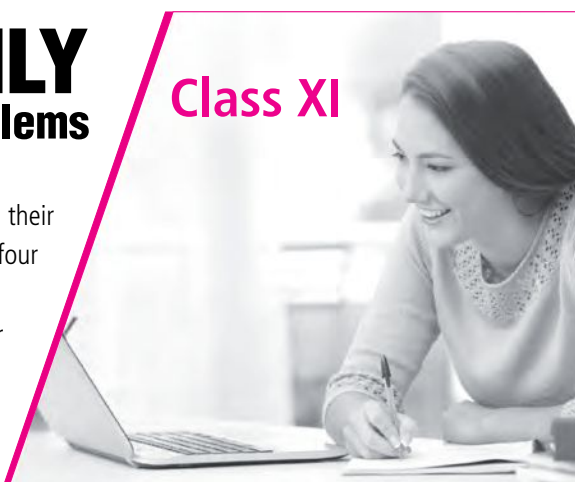
Some Basic Concepts of Chemistry

Total Marks : 120

Time Taken : 60 Min.

NEET / AIIMS

Only One Option Correct Type

1. 4 g carbon was heated with 8 g of sulphur. The percentage purity of carbon disulphide (CS_2) in the final product obtained is
   (a) 59.2% (b) 69.2%
   (c) 79.2% (d) 89.2%

2. A certain amount of a metal whose equivalent mass is 27.9 g mol^{-1} displaces 700 mL of H_2 measured at standard conditions from an acid. Hence, mass of the metal is
   (a) 1.74 g (b) 0.87 g
   (c) 3.78 g (d) 9.77 g

3. Mole fraction of I_2 in C_6H_6 is 0.2. What would be the molality of I_2 in C_6H_6?
   (a) 4.208 m (b) 3.205 m
   (c) 6.02 m (d) 5.42 m

4. O_2 gas produced by the decomposition of 2.45 g of $KClO_3$, is completely reacted with H_2 gas obtained by the reaction of zinc and dil. H_2SO_4. What weight of zinc is required for the production of this H_2 gas?
   (Given : Molar mass of $KClO_3$ = 122.5 g mol^{-1},
   Zn = 65 g mol^{-1})
   (a) 1.3 g (b) 2.6 g (c) 3.9 g (d) 5.2 g

5. Acidified $KMnO_4$ oxidises oxalic acid to CO_2. What is the volume (in litres) of 10^{-4} M $KMnO_4$ required to completely oxidise 0.5 L of 10^{-2} M oxalic acid in acidic medium?
   (a) 125 (b) 1250 (c) 200 (d) 20

6. 250 mL of 0.5 M sodium sulphate (Na_2SO_4) solution is added to an aqueous solution containing 10.0 g of $BaCl_2$ resulting in the formation of white precipitate of $BaSO_4$. How many grams of barium sulphate will be obtained?
   (a) 10.62 g (b) 11.18 g (c) 9.02 g (d) 13.4 g

7. One gram of calcium was burnt in excess of oxygen and the oxide formed was dissolved in water to make one litre solution. The normality of the solution is
   (a) 0.03 N (b) 0.01 N (c) 0.04 N (d) 0.05 N

8. A blackened silver coin weighing 15 g on treatment with HCl yielded 25 mL of H_2S at 12°C and 775 mm pressure. What percentage of the original silver tarnished?
   (a) 1.57% (b) 2.35% (c) 3.07% (d) 1.25%

9. Excess of carbon dioxide is passed through 50 mL of 0.5 M calcium hydroxide solution. After the completion of the reaction, the solution was evaporated to dryness. The solid calcium carbonate was completely neutralised with 0.1 N hydrochloric acid. The volume of hydrochloric acid required is (Atomic mass of calcium = 40 g mol^{-1})
   (a) 200 mL (b) 500 mL (c) 400 mL (d) 300 mL

10. 1.325 g of anhydrous sodium carbonate is dissolved in water and the solution is made upto 250 mL. On titration, 25 mL of this solution neutralises 20 mL of a solution of sulphuric acid. How much water should be added to 450 mL of this acid solution to make it exactly N/12?
    (a) 250 mL (b) 275 mL (c) 225 mL (d) 235 mL

11. 2.6 g of a mixture of calcium carbonate and magnesium carbonate is strongly heated to a constant weight of 1.3 g. The atomic weights of calcium and magnesium are 40 and 24 respectively. What is the weight of calcium carbonate in the original mixture?
    (a) 980 mg   (b) 400 mg
    (c) 1.75 g   (d) 0.74 g

12. Manganese trifluoride can be prepared by the reaction :

    $$MnI_2 + 13/2\ F_2 \longrightarrow MnF_3 + 2IF_5$$

    What is the minimum amount of F_2 that must be used to react with 12 g of MnI_2, if only 75% F_2 is utilised to convert all of the MnI_2 to MnF_3?
    (a) 12.78 g   (b) 13.63 g
    (c) 9.54 g   (d) 11.77 g

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** 10,000 molecules of CO_2 have the same volume at STP as 10,000 molecules of CO at STP.
    Reason : Both CO and CO_2 are formed by combustion of carbon (coke) in presence of oxygen.

14. **Assertion :** At STP, 1 mL of ideal gas contains 2.69×10^{19} molecules.
    Reason : One mole of a gas is the amount of gas which has a volume of 22.4 litres at STP.

15. **Assertion :** In a gaseous reaction, the ratio by volumes of reactants and gaseous products is in agreement with their molar ratio.
    Reason : Volume of gas is inversely proportional to its number of moles at a particular temperature and pressure.

JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

16. 1 mole of BaF_2 is treated with 2 moles of H_2SO_4. To make the resulting mixture neutral, NaOH is added. The amount of NaOH required is
    (a) 4 mol (b) 2 mol (c) 3 mol (d) 1 mol

17. 10.1 g of KNO_3 is dissolved in 500 mL of H_2O. Mass of $Ba(NO_3)_2$ that should be added to this solution to get a molality (m) of 0.3 m with respect to NO_3^- ion is
    (Mol wt. of KNO_3 = 101 g mol^{-1},
    Mol wt. of $Ba(NO_3)_2$ = 261 g mol^{-1})
    (a) 1.3 g   (b) 13 g   (c) 6.5 g   (d) 65 g

18. P_4O_6 and P_4O_{10} are formed by burning P_4 with O_2 as :

    $$P_4 + 3O_2 \longrightarrow P_4O_6$$
    $$P_4 + 5O_2 \longrightarrow P_4O_{10}$$

    What are the masses of P_4O_6 and P_4O_{10} respectively that will be produced by the combustion of 2.0 g of P_4 in 2.0 g of oxygen leaving no P_4 and O_2?
    (a) 1.125 g, 1.296 g   (b) 1.996 g, 2.004 g
    (c) 2.004 g, 1.996 g   (d) 1.296 g, 1.125 g

19. A 10 mL solution of hydrogen peroxide is diluted to 250 mL with distilled water. 25 mL of this diluted solution when titrated against 1.023 N/10 $KMnO_4$ solution, required 13.32 mL of $KMnO_4$ solution. Volume strength of H_2O_2 solution is
    (a) 76.16   (b) 30.464   (c) 3.046   (d) 7.616

More than One Options Correct Type

20. 10 g of ammonium chloride is mixed with 10 g of slaked lime and the mixture is heated. Then
    (a) 3.1 g of NH_4Cl will be left unreacted
    (b) 10.4 g of $CaCl_2$ will be formed
    (c) 2.3 g of NH_3 will be formed
    (d) NH_4Cl will be the limiting reactant.

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						^{1}X		^{2}C			^{3}E		
^{4}G	A	L	A	C	T	A	N	^{5}A	R	G	O	N	^{6}M	T
^{7}Z	U	S	A	M	M	E	N		A		O	H
	^{8}T	H	E	R	M	I	T	E	^{9}M	^{10}C	^{11}R	E	N	A	^{12}T	I	^{13}O	N
^{14}T							H		E	E	O		O	N	H		X
E		^{15}E	F	F	U	S	I	O	N	S	R	N		C	A		O
P				^{16}A			P	^{17}D	O	V	G		H	L	L		N
H				C			H	R	M	A	A		R		L		E
I	^{19}F	^{18}L	U	I	D	I	T	Y	I	O	T	L		O		I
G	R			D				^{20}C	L	K	R	I	I	^{21}C	M		U	^{22}T
R	E			V				A	L	O	P	O	T	H	A		M	R
A	O			A				S		L	^{23}H	N	E	A	^{24}T	A	X	O	L
P	N			^{25}L	A	C	T	I	D	E		R	I		N
H				U			I		R		^{26}A	C	C	^{27}U	R	A	C	Y
^{28}C	O	P	P	E	R		R			T	O		R
	^{29}P	O	S	I	T	R	O	N	S	Z		A	E
^{30}M	U	L	L	I	K	E	N				L	A

21. A mixture of sodium iodide and sodium chloride when treated with sulphuric acid gave sodium sulphate equal to the weight of the original mixture. Which of the following could not be the correct percentage composition of the mixture?
(a) 28.86%, 71.14 % (b) 24.56%, 75.44%
(c) 36.39%, 63.61% (d) 27.85%, 72.15%

22. The atomic weights of two elements A and B are 20 and 40 respectively. Which of the following statements are correct for these two elements?
(a) x g of A contains y atoms which is equal to atoms present in x g of B.
(b) x g of A contains y atoms which is equal to atoms present in $2x$ g of B.
(c) At STP, x L of monoatomic gas A is equal to x L of monoatomic gas B.
(d) At STP, x L of monoatomic gas A weighs y g and y L of monoatomic gas B is measured x g.

23. The number of molecules in 11 g of CO_2 is same as that in
(a) 8 g of O_2 (b) 16 g of O_2
(c) 7 g of CO (d) 3.5 g of CO

Integer Answer Type

24. The ratio of molecular mass to empirical formula mass of a hydrocarbon having 92.4% C and vapour density 39 is

25. The number of gram atoms of non-metal atoms present in 0.5 mole of potassium ferrocyanide is

26. In an experiment, 4 g of M_2O_x oxide was reduced to 2.8 g of the metal. If the atomic mass of the metal is 56 g mol^{-1}, the number of O atoms in the oxide is

Comprehension Type

The percentage labelling of oleum (mixture of H_2SO_4 and SO_3) refers to the total mass of pure H_2SO_4. The total amount of H_2SO_4 found after adding calculated amount of water to 100 g oleum is the percentage labelling of oleum. Higher the percentage labelling of oleum, higher is the amount of free SO_3 in the oleum sample.

27. What is the amount of free SO_3 in an oleum sample labelled as '118%'?
(a) 40% (b) 50% (c) 70% (d) 80%

28. 100 g sample of '147%' oleum was taken and calculated amount of H_2O was added to make H_2SO_4 solution. 500 mL of x M KOH solution is required to neutralise the H_2SO_4 solution. The value of x is
(a) 1 (b) 2 (c) 4 (d) 6

Matrix Match Type

29. Match the Column I with Column II and mark the appropriate choice.

Column I	Column II
(A) Molarity (M)	(P) Temperature
(B) Molality (m)	(Q) Pressure
(C) Mole fraction (x)	(R) Dilution
(D) Normality (N)	(S) Volume

	A	B	C	D
(a)	P, Q, R	P, R	Q, R	P, Q
(b)	P, Q, R, S	Q, R	Q, R	P, Q, R, S
(c)	P, Q, R, S	P, Q	P, R	P, Q, S
(d)	P, Q, S	P, R	Q, S	Q, S

30. Match the mass of elements given in Column I with the no. of moles/atoms given in Column II and mark the appropriate choice.

Column I	Column II
(A) 28 g of He	(P) 2 moles
(B) 46 g of Na	(Q) 9.03×10^{23} atoms
(C) 60 g of Ca	(R) 7 moles
(D) 27 g of Al	(S) 1 mole
	(T) 42.16×10^{23} atoms
	(U) 1.5 moles

	A	B	C	D
(a)	P, R, T	Q, S	Q, P	P
(b)	Q, T	P, Q	R, T	S
(c)	U	Q, R	T, U	P, T
(d)	R, T	P	Q, U	S

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SELF CHECK ✏

Check your score! If your score is

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

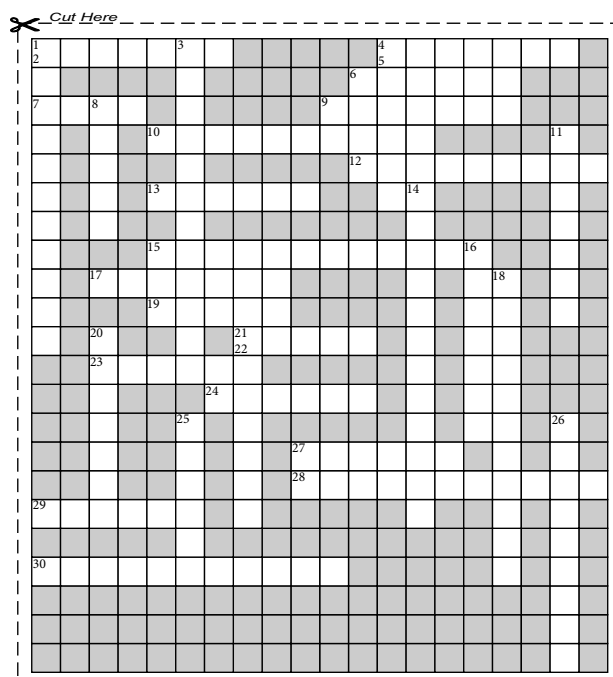| > 90% | EXCELLENT WORK ! | You are well prepared to take the challenge of final exam. |
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CROSS WORD
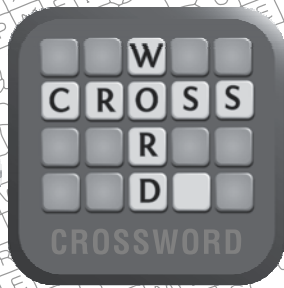
Readers can send their responses at editor@mtg.in or post us with complete address by 25th of every month to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.

ACROSS

1. Glucoside of indigo, an important vat dye. (7)
4. Mixture of evenly dispersed substances. (7)
6. Fundamental particles that make up proton and neutron. (6)
7. An almost non-crystalline form of quartz or hydrated silica, used as gemstone. (4)
9. Most stable form of calcium carbonate, which is also a principal constituent of limestone and marble. (7)
10. _____ modified Bohr's theory and gave the concept of elliptical orbits. (10)
12. SI unit of radioactivity. (9)
13. Solid left behind when urea is heated. (6)
15. _____ is used to prepare alkene by heating quaternary ammonium hydroxides. (12)
17. A man-made element of the actinide series discovered in 1953. (7)
19. The most popular trade name of polycarbonate. (5)
21. Naturally occurring mineral form of aluminium oxide which is used to make abrasive powder. (5)
23. The common name of 4-methoxybenzyl group, a versatile protecting group for primary alcohols. (6)
24. The enzyme used during hydrolysis of ester to form carboxylic acid and alcohol. (6)
27. Shape of $IO_2F_2^-$. (6)
28. A 4% solution of an inorganic acid in water, used as an antiseptic and eye wash. (11)
29. A resin formed by copolymerisation of melamine and formaldehyde. (6)
30. The process of converting CO or CO_2 to methane by catalytic reaction with hydrogen under pressure. (11)

DOWN

2. A regular geometry of a crystal with 20 faces, 12 vertices and 30 edges. (11)
3. Conformational isomers which can be separated due to restricted rotation. (12)
5. Recycled or broken glass pieces added during glass making. (6)
8. Crude potassium hydrogen tartrate obtained from wine and used in dye industries. (5)
11. Common name of bicyclo [4.4.0] decane, usually obtained by catalytic hydrogenation of naphthalene. (7)
14. A dye obtained by the oxidation of aniline hydrochloride. (12)
16. The name given to pure metal lumps. (7)
18. The addition of an oxygen bridge across a double bond to give an oxirane. (11)
20. A brown substance formed by heating sugar above its melting point. (7)
22. An alloy of chromium, iron and nickel, used for making hairsprings for watches and clocks. (7)
25. A homopolysaccharide consisting of glucose monomeric units. (6)
26. An occupational disease of those who work with white phosphorus. (9)

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