

TIFR - CHEMISTRY MOCK TEST PAPER

- Attempt All the 40 Questions (Objective).
- Each questions carries three marks.
1 negative mark for each wrong answer.
- Pattern of questions : MCQs
- Total marks : 120
- Duration of test : 3 Hours

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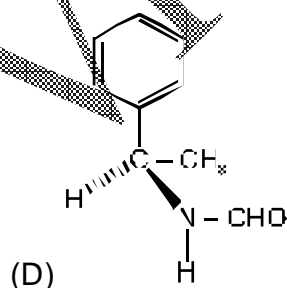
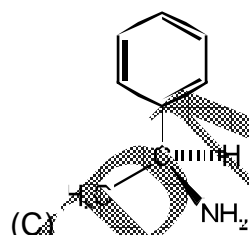
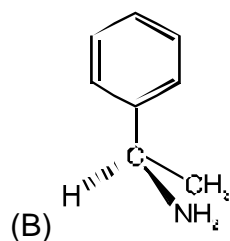
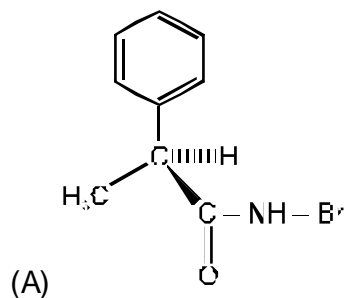
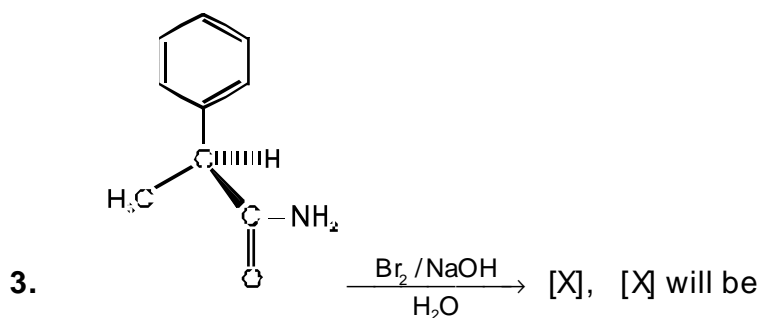
Page 1

Some Useful DataAvogadro number = $6.02 \times 10^{23} \text{ mol}^{-1}$ $e = 1.6 \times 10^{-19} \text{ C}$ $RT/F = 0.0257 \text{ V at } 25^\circ\text{C}$ $h = 6.626 \times 10^{-34} \text{ Js}$

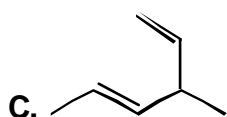
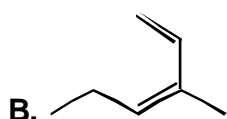
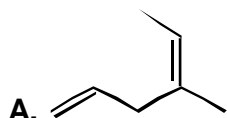
Faraday = 96500 C/eq. wt

 $c = 3 \times 10^8 \text{ ms}^{-1}$ Boltzmann constant $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$ Mass of an electron = $9.109 \times 10^{-31} \text{ kg}$ Standard reduction potential of $\text{Cu}^{2+} + 2e^- \leftrightarrow \text{Cu}$: +0.34 V at 25°C Standard reduction potential of $\text{Ag}^+ + e^- \leftrightarrow \text{Ag}$: +0.80 V at 25°C K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$ $S = k \ln W$

- The molar absorptivity at λ_{max} is minimum for
 - $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- Which of the following has maximum lattice energy?
 - Li_2O
 - Na_2O
 - MgO
 - BaO



4. The pK_1 and pK_2 values for alanine are 2.34 and 9.60 respectively. What is its isoelectric point?
- (A) 5.97
(B) 2.34
(C) 9.60
(D) 7.26
5. Which one among the dienes **A to D** will undergo [3,3]-sigmatropic shift upon heating



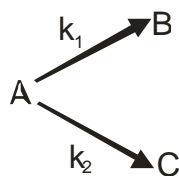
(A) A

(B) B

(C) C

(D) D

6. A substance undergoes first order decomposition involving two parallel first order reactions as –



$$k_1 = 1.25 \times 10^{-4} \text{ s}^{-1}$$

$$k_2 = 3.80 \times 10^{-5} \text{ s}^{-1}$$

The mol percent of B in the products is

- (A) 23.17
- (B) 76.83
- (C) 30.16
- (D) 69.84

7. Half life of the reaction is independent of initial concentration of H_2O_2 . Volume of O_2 gas after 20 minutes is 5L at 1 atm and 27°C and after completion of the reaction 50L. The rate constant is:-

- (A) $\frac{1}{20} \log_{10} \text{min}^{-1}$
- (B) $\frac{2.303}{20} \log_{10} \text{min}^{-1}$
- (C) $\frac{2.303}{20} \log_{\frac{50}{45}} \text{min}^{-1}$
- (D) $\frac{2.303}{20} \log_{\frac{45}{30}} \text{min}^{-1}$

8. Chromium metal can be electrolytically plated out from an acidic solution containing CrO_3 . Assuming that all of the CrO_3 is in a soluble form, how many coulombs are required to cause 3.68 g of Cr to be deposited on the cathodic electrode?

- (A) 20,600 coul
- (B) 41,000 coul
- (C) 10,250 coul

(D) 61,500 coul

9. The proton NMR spectrum of a compound with molecular formula C_2H_6O was obtained. Under low resolution three signals with relative intensities of 1 : 2 : 3 were recorded. Under high resolution, the high field signal split into three lines of relative intensities 1 : 2 : 1, medium field signal into four lines of intensities in the ratio of 1 : 3 : 3 : 1. What is the structural formula?

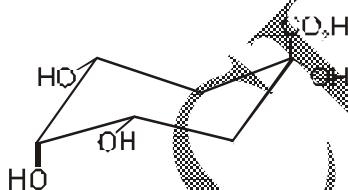
(A) CH_3CH_2OH

(B) CH_3OCH_3

(C) CH_3CHO

(D) Both A & B

10. The following molecule has a



(A) Centre of symmetry

(B) Plane of symmetry

(C) Axis of symmetry

(D) None of the above

11. The correct order of increasing $[H_3O^+]$ in the following aqueous solutions is:

(A) $0.01\text{ M } H_2S < 0.01\text{ M } H_2SO_4 < 0.01\text{ M } NaCl < 0.01\text{ M } NaNO_2$

(B) $0.01\text{ M } NaCl < 0.01\text{ M } NaNO_2 < 0.01\text{ M } H_2S < 0.01\text{ M } H_2SO_4$

(C) $0.01\text{ M } NaNO_2 < 0.01\text{ M } NaCl < 0.01\text{ M } H_2S < 0.01\text{ M } H_2SO_4$

(D) $0.01 \text{ M H}_2\text{S} < 0.01 \text{ M NaNO}_2 < 0.01 \text{ M NaCl} < 0.01 \text{ M H}_2\text{SO}_4$

12. Which statement/relationship is correct?

(A) Upon hydrolysis salt of a strong base and weak acid gives a solution with $\text{pH} < 7$

(B) $\text{pH} = -\log \frac{1}{[\text{H}^+]}$

(C) Only at 25°C the pH of water is 7

(D) The value of pK_w at 25°C is 7

13. If the ionic strength of $\text{Cd}(\text{NO}_3)_2 = 1$ unit, then the molality of $\text{Cd}(\text{NO}_3)_2$ solution will be.

(A) 1 unit

(B) 1/2 unit

(C) 1/3 unit

(D) 1/4 unit

14. Electrolysis of a solution of HSO_3^- ions produces $\text{S}_2\text{O}_8^{2-}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole of $\text{S}_2\text{O}_8^{2-}$ per hour –

(A) + 71.5 amp

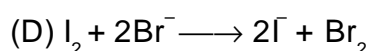
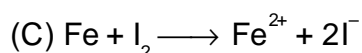
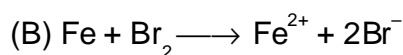
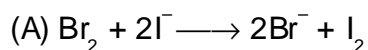
(B) 35.7 amp

(C) 142.96 amp

(D) 285.93 amp

15. $2e^-$, standard oxidation potential = -1.09 volt. For $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^-$,

standard oxidation potential = +0.44 volt. Which of the following reactions is non-spontaneous –



16. Consider the following statements about intermolecular and intramolecular hydrogen bonds

- (1) Both types of H-bonds are temperature-dependent
- (2) Intramolecular H-bond disappears on increasing the concentration
- (3) Intermolecular H-bond disappears on decreasing the concentration
- (4) The boiling points of compounds having intramolecular H-bond are lower than that of those compounds which have intermolecular H-bond

Which of the statements given above are correct?

(A) 1, 2 and 4

(B) 3 and 4

(C) 1, 3 and 4

(D) 1 and 2

17. 100 mL of tap water containing $\text{Ca}(\text{HCO}_3)_2$ was titrated with N/50 HCl with methyl orange as indicator. If 30 mL of HCl were required, calculate the temporary hardness as parts of CaCO_3 per 10^6 parts of water.

(A) 150 ppm

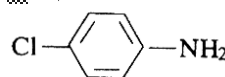
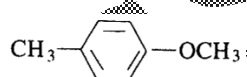
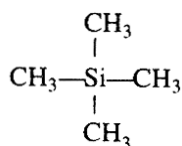
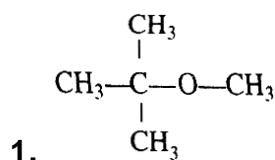
- (B) 300 ppm
- (C) 450 ppm
- (D) 600 ppm
18. Which of the following reactions takes place at elevated temperature (500 – 550°C) and high pressure in the presence of a catalyst?
- (A) Hydrogen reacts with oxygen to form water
- (B) Hydrogen reacts with Nitrogen to form Ammonia
- (C) Saturation of ethylene to ethane by hydrogen
- (D) None of these
19. The product formed, when $\text{Mg}(\text{NH}_4)\text{PO}_4$ is heated is
- (A) $\text{Mg}(\text{NH}_4)_2\text{PO}_4$
- (B) MgO
- (C) PbO
- (D) $\text{Mg}_2\text{P}_2\text{O}_7$
20. The solubility of hydroxides, fluorides or oxalates of the metals of Group II A
- (A) Increase down the group
- (B) Decreases down the group
- (C) Varies randomly
- (D) Is constant
21. Gradual addition of potassium iodide solution to $\text{Bi}(\text{NO}_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Identify the yellow precipitate.

- (A) I_2
- (B) KI_3
- (C) $Bi(OH)_2$
- (D) $Bi(OH)(NO_3)_2$
22. An unknown inorganic compound (X) loses its water of crystallization on heating and its aqueous solution gives the following reactions :
- (a) It gives a white turbidity with dilute HCl solution
- (b) It decolorizes a solution of iodine in potassium iodide
- (c) It gives a white precipitate with silver nitrate solution which turns black on standing. Identify the compound (X)
- (A) $Na_2CO_3 \cdot 10H_2O$
- (B) $Na_2S_2O_3 \cdot 5H_2O$
- (C) $Na_2SO_4 \cdot 10H_2O$
- (D) None of these
23. In photography, sodium thiosulphate is used for
- (A) Softening very dark images
- (B) Making the latent image visible
- (C) Intensifying faint images
- (D) Dissolving residual silver bromide
24. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is
- (A) $LiCl > NaCl > KCl$

- (B) $\text{KCl} > \text{NaCl} > \text{LiCl}$
- (C) $\text{NaCl} > \text{KCl} > \text{LiCl}$
- (D) $\text{LiCl} > \text{KCl} > \text{NaCl}$
25. Identify the least stable ion amongst the following
- (A) Li^+
- (B) Be^-
- (C) B^-
- (D) C^-
26. According to band theory of bonding, conduction occurs in very good conductors because
- (A) Valence band is full
- (B) Valence band and conduction band overlap
- (C) Band gap is appreciable
- (D) Band gap is small
27. Which of the following, when doped into a crystal of ultra purified Germanium, will convert it into a *p*-type semiconductor?
- (A) C
- (B) As
- (C) In
- (D) Na
28. In the mass spectrum of ethyl benzene some of the prominent peaks appear at $m/e = 106, 91$ and 65 . Which of the species given below is not responsible for these peaks?

- (A) Ethyl benzene
- (B) Ethene
- (C) Tropylium ion ($C_7H_7^+$)
- (D) $C_5H_5^+$

29. How many signals in NMR spectra will be obtained from the following compounds respectively?



- (A) 2, 1, 3, 2
 - (B) 1, 4, 3, 2
 - (C) 2, 3, 1, 2
 - (D) 1, 1, 2, 1
30. If the enthalpy of a reversible reaction is $8.314 \text{ kJ mol}^{-1}$ over the temperature range 400-500 K, the value of $\ln K_{500}/K_{400}$ for the reaction is –
- (A) 1.0
 - (B) 2.0
 - (C) 2.5
 - (D) 0.5
31. The hydrogen ion concentration of a slightly acidic water solution can be represented by:-
- (A) $14 - \text{pOH}$

(B) K_w/pOH

(C) 10^{-pOH}

(D) $10^{-(14 - pOH)}$

32. If v is the volume of a gas adsorbed on the surface of a solid, the plot of p/v versus p where p is the gas pressure in the langmuir adsorption isotherm, gives a straight line with slope equal to

(A) $\frac{p}{v}$

(B) K

(C) $\frac{1}{Kv_{mono}}$

(D) $\frac{1}{v_{mono}}$

33. The equilibrium constant for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 32 at a given temperature. The equilibrium concentrations of I_2 and HI are 0.5×10^{-3} and 8×10^{-3} M respectively. The equilibrium concentration of H_2 is –

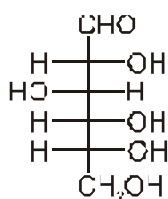
(A) 1×10^{-3} M

(B) 0.5×10^{-3} M

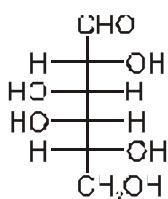
(C) 2×10^{-3} M

(D) 4×10^{-3} M

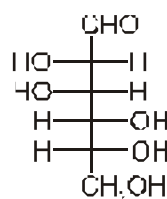
34. Which of the statement regarding following structures is true ?



I



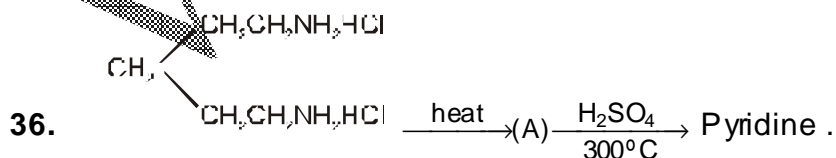
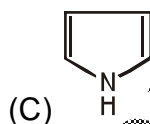
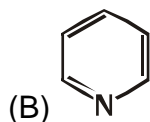
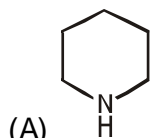
II



III

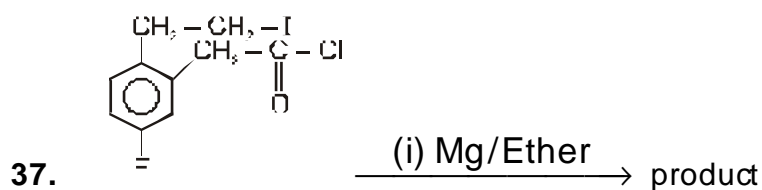
- (A) I and II are epimers
 (B) I and III are epimers
 (C) Both are true
 (D) All the three are epimers

35. Among the given compounds, the one which is least basic is

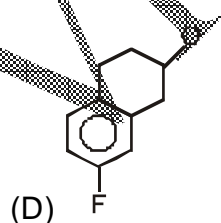
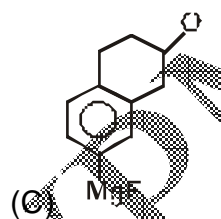
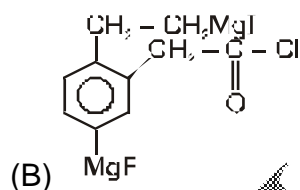
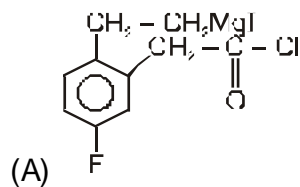


The compound (A) is :

- (A) Piperidine
- (B) Pyrrole
- (C) 3-methyl pyridine
- (D) None of these



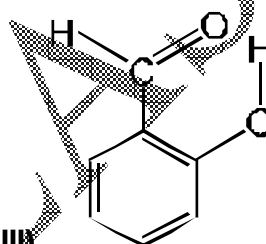
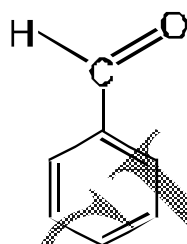
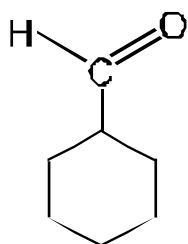
The final product of the reaction is



38. Acetic acid show two signals a and b at $\delta = 8.0$ ppm and 3.8 ppm, respectively in a 50 MHz NMR spectrometer. Calculate the separation in frequency between the two signals on a 300 MHz spectrometer.

- (A) $\Delta\nu_a = 2400$ Hz
 (B) $\Delta\nu_b = 1140$ Hz
 (C) A & B both
 (D) $\Delta\nu_a = 2400$ MHz & $\Delta\nu_b = 1140$ MHz

39. The order of the frequency of the carbonyl absorption in the aldehydes given below is:



- (A) I > III > II
 (B) II > III > I
 (C) III > II > I
 (D) I > II > III

40. Thermal reaction of allyl phenyl ether generates a mixture of ortho- and para-allyl phenols. The para-allyl phenol is formed via

- (A) a [3, 5]-sigmatropic shift
 (B) First ortho-allyl phenol is formed, which then undergoes a [3, 3]-sigmatropic shift
 (C) Two consecutive [3, 3]-sigmatropic shifts
 (D) Dissociation to generate allyl cation, which then adds at para-position

ANSWER KEY

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Answer	A	C	C	A	B	B	C	B	A	B	C	C	C	A	D	C	B	B	D	A
Question	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Answer	B	B	D	B	B	B	C	B	A	D	D	D	D	C	C	B	C	D	B	B

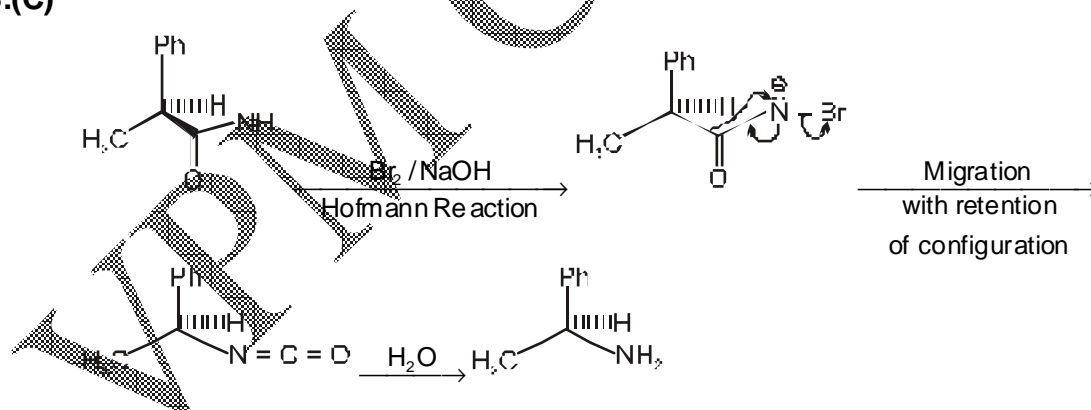
HINTS AND SOLUTION

1.(A) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+} = \text{Mn}^{+2} = 3d^5$

In $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ complex all transitions are not only laporte forbidden but also spin forbidden. Absorptions associated with doubly forbidden transitions are extremely weak with extinction coefficients several times smaller than those for singly forbidden transitions. So the molar absorptivity at λ_{max} is minimum for $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$.

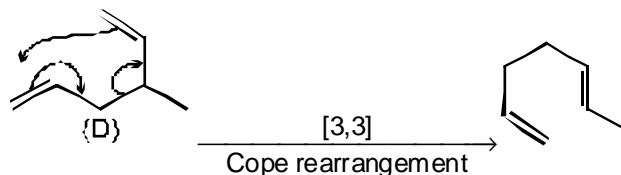
2.(C) MgO, Mg^{2+} ion is smallest in size and double the charge in comparison to Li^+ and Na^+ ions.

3.(C)



4. (A) $\text{pI} = \frac{\text{pK}_1 + \text{pK}_2}{2} = \frac{2.34 + 9.60}{2} = \frac{11.94}{2} = 5.97$

5.(B) The thermal rearrangement of 1, 5-dienes by [3,3] sigmatropy is called cope rearrangement.



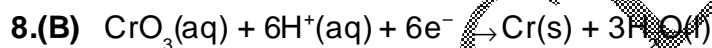
$$6.(B) \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4} \times 100}{1.25 \times 10^{-4} + 3.80 \times 10^{-5}} = 76.83$$

7.(C) $t_{\frac{1}{2}}$ is independent of initial concentration a, for first order reaction.

$$x \propto V_t \quad (= 5L \text{ at } t = 20 \text{ minutes})$$

$$a \propto V_f \quad (= 50 L \text{ at completion})$$

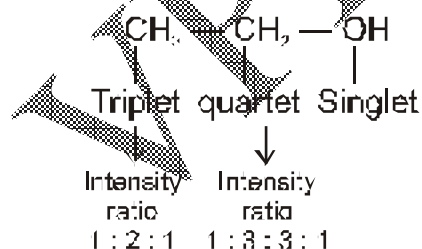
$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{20} \log \frac{50}{45}$$

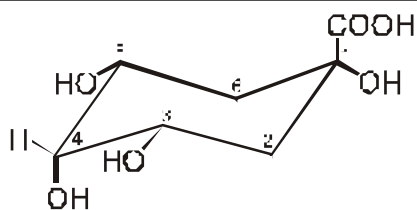


$$\text{Coulombs} = (3.68 \text{ g Cr}) \times \left(\frac{1 \text{ mol Cr}}{52.0 \text{ g Cr}} \right) \left(\frac{6\text{F}}{1 \text{ mol Cr}} \right) \times \left(\frac{96,500 \text{ C}}{1 \text{ F}} \right) = 41,000 \text{ coulombs}$$

9.(A) Structural formula $\text{CH}_3 - \text{CH}_2 - \text{OH}$

relative intensities 3 : 2 : 1





10.(B)

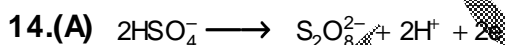
The cyclohexane ring has one plane of symmetry across 1, 4 positions, cutting all 4 substituents in to half. The similar groups in cis orientation at 1, 3 positions also show plane of symmetry.

11.(C) H_2SO_4 is strong acid having $\text{pH} < 7$. NaNO_2 on hydrolysis gives alkaline solution of $\text{pH} > 7$. NaCl is neutral and H_2S is weak acid.

12.(C) Hydrolysis of a salt of strong base and weak acid gives $\text{pH} > 7$.

Also, $\text{pH} = \log \frac{1}{[\text{H}^+]}$ and K_w for H_2O at $25^\circ\text{C} = 10^{-14}$. The pH of pure water is 7 at 25°C and decreases with increases in temperature.

13.(C) $I = \frac{1}{2}(2^2b + 1^2 \cdot 2b) = 3b = 1 \Rightarrow b = 1/3 \Rightarrow C$



$$\frac{2F}{0.75} \longrightarrow 1 \text{ mole } \text{S}_2\text{O}_8^{2-}$$

$$\therefore I = \frac{\frac{2}{0.75} \times 96500}{3600} = 71.5 \text{ amp}$$

15.(D) E° for reaction in (d) = $E_{\text{OP}_1}^\circ + E_{\text{RP}_1}^\circ = -1.09 + (-0.54) = -1.63 \text{ V}$

Since, E° is negative and thus, reaction is non-spontaneous.

16.(C) (1) Both type of H-bonds break on heating so there are temperature dependent.

(2) Intramolecular H-bond is independent of concentration.

(3) Intermolecular H-bonds increase on increasing concentration and decrease on decreasing concentration.

(4) (a) Boiling point (BP) $\propto \frac{1}{\text{Intramolecular H-bond}}$

(b) B.P. \propto Intermolecular H-bond.

17.(B) 30 mL N / 50 HCl \equiv 30 mL / N/50 Ca (HCO₃)₂ \equiv 30 mL N / 50 CaCO₃ \equiv 100 mL tap water

$$\text{Mass of CaCO}_3 \text{ in 100 mL tap water} = \frac{E \times N \times V}{1000} = \frac{50 \times 30}{50 \times 1000} = 0.03 \text{ g}$$

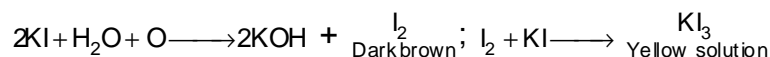
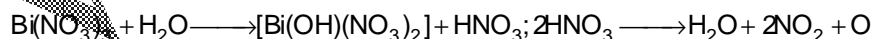
\Rightarrow hardness = 300 ppm

18.(B) The first reaction (a) occur on electrical sparking. The reaction in (c) occurs at elevated temperatures in the presence of a catalyst but not at 500 – 550°C. The correct option is (b) which occurs at the above conditions.

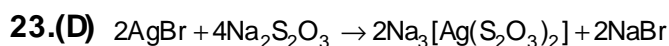
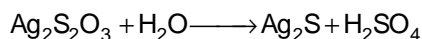
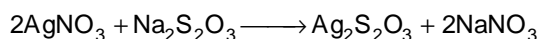
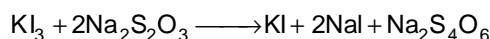
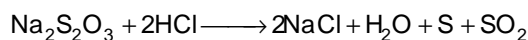
19.(D) $2\text{Mg}(\text{NH}_4)\text{PO}_4 \xrightarrow{\text{O}}$ $\text{Mg}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} + 2\text{NH}_3$

20.(A) Both lattice energy and hydrolysis energy decreases moving down the group due to gradual increase in size of M⁺⁺ ion. So formed tends to increase the solubility while latter tends to decrease it. But lattice energy has dominating role here. And therefore solubility increases down the group.

21.(B) At first, Bi(NO₃)₃ undergoes hydrolysis. Nitric acid is formed. Which oxidises KI to iodine. The liberated iodine dissolves in KI to form yellow solution of KI₃.



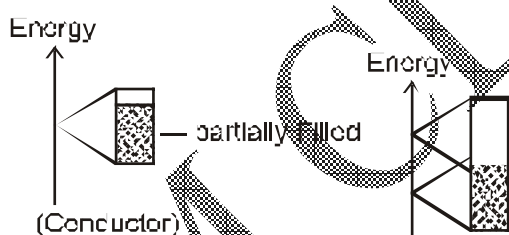
22.(B) X = Na₂S₂O₃·5H₂O



24.(B) The ease of ionization of the given compounds will be in the order $\text{LiCl} < \text{NaCl} < \text{KCl}$, hence equivalent conductance at infinite dilution in the same order.

25.(B) Be^- is attaining $2s^2 2sp^1$ configuration by losing its fulfilled stability of $2s^2$ configuration.

26.(B) A/C to band theory in electrical conductors either the valence band is only partially full or valence and conduction bands overlap.

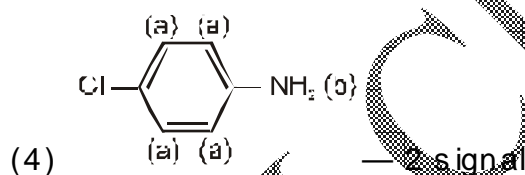
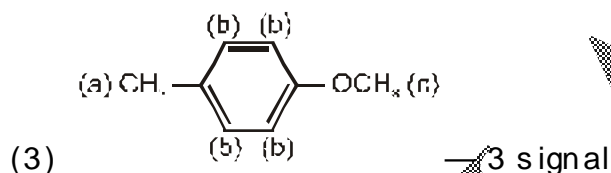
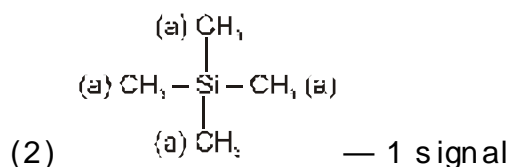
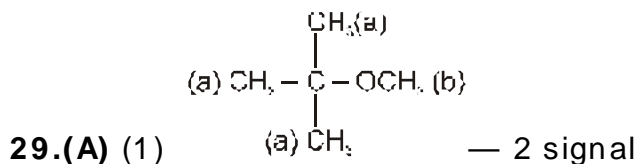


27.(C) Purified Silicon (or germanium) crystals can be converted to p-type or n-type semiconductor by high temperature diffusion of the appropriate dopant element upto a concentration of 1 part in 10^8 Group III elements boron,

Aluminium gallium or indium can be used to make p-type semiconductors. Though indium is the most used because of its low melting point.

28.(B) The peak at $m/e = 106$ is the molecular ion peak. because molecular mass of $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ (ethyl benzene) is 106. The peak at $m/e = 91$ is due to stable benzyl ion or more likely due to tropylium ion (C_7H_7^+). It is the base

peak. The peak at $m/e = 65$ may be due to removal of acetylene molecule ($C_2H_2 = 26$ mass units) from tropylium ion.



30.(D)
$$\ln \frac{K_2}{K_1} = \frac{\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) = \frac{8314 \times 10^3 \times (500 - 400)}{8314 \times 400 \times 500} = 0.5$$

31.(D)
$$pH = -\log[H^+]$$

$$[H^+] = 10^{-14}$$

$$pH + pOH = 14$$

$$pH = 14 - pOH$$

$$[H^+] = 10^{-(14 - pOH)}$$

32.(D) According to langmuir isotherm

$$Q = \frac{K_p}{(1+K_p)}$$

$$\frac{1}{Q} = 1 + \frac{1}{K_p}$$

$$Q = \frac{v}{v_{\text{mono}}}$$

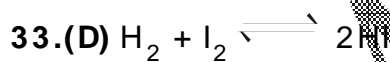
$$\frac{v}{v_{\text{mono}}} = 1 + \frac{1}{K_p}$$

Multiplying through out by $\frac{p}{v_{\text{mono}}}$

$$\frac{p}{v} = \frac{p}{v_{\text{mono}}} + \frac{1}{Kv_{\text{mono}}}$$

$$y = mx + C$$

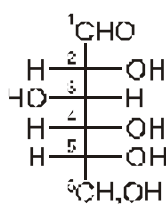
$$\text{Slope} = \frac{1}{v_{\text{mono}}}$$



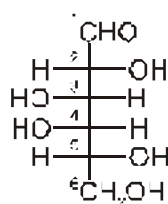
$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$[\text{H}_2] = \frac{[\text{HI}]^2}{[\text{I}_2] \times K} = \frac{(8 \times 10^{-3})^2}{(0.5 \times 10^{-3})(32)} = 4 \times 10^{-3} \text{ M}$$

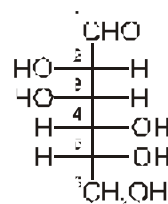
34.(C) Epimers are a pair of diastereomers which differ only in the configuration around a *single carbon* atom



I (glucose)



II (galactose)



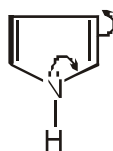
III (Mannose)

Note that (i) Structures I and II differ only at C₄;

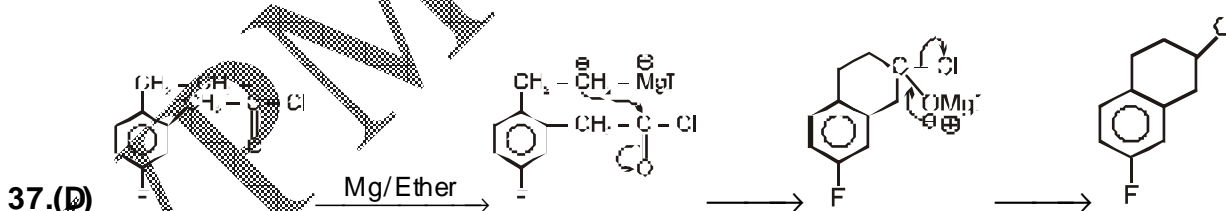
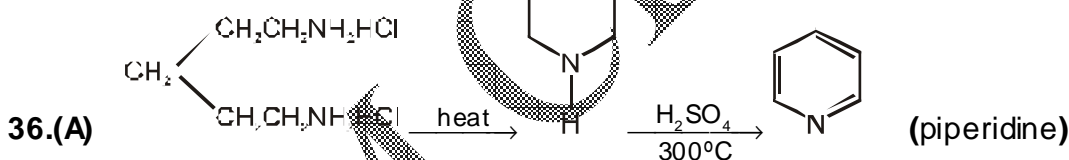
(ii) Structures II and III differ at C₂ and C₄;

(iii) Structures I and III differ only at C₂

Thus structures I and II and I and III are epimers



35.(C) C1CCNC1 is least basic due to less availability of lone pair.



38.(C) $\Delta v_a \times v_0 = 8 \times 10^{-6} \times 300 \times 10^6 = 2400 \text{ Hz}$

$$\Delta v_b = \delta_b \times v_0 = 3.8 \times 10^{-6} \times 300 \times 10^6 = 1140 \text{ Hz}$$

39.(D) (i) Cyclohexane carboxaldehyde being saturated will absorb around 1730cm^{-1} .

(ii) In benzaldehyde the absorption will be shifted to lower frequency (1700 cm^{-1}) due to conjugation.

(iii) In salicylaldehyde the internal (chelate) hydrogen bonding causes a further large frequency shift to around 1666 cm^{-1} .

40.(B)

