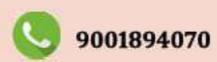


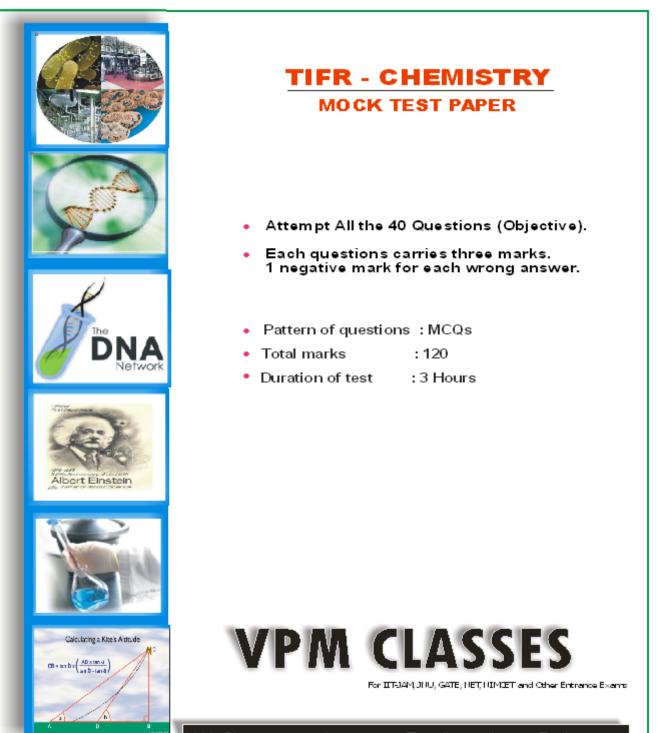
# TIFR CHEMISTRY SOLVED SAMPLE PAPER

# **\* DETAILED SOLUTIONS**









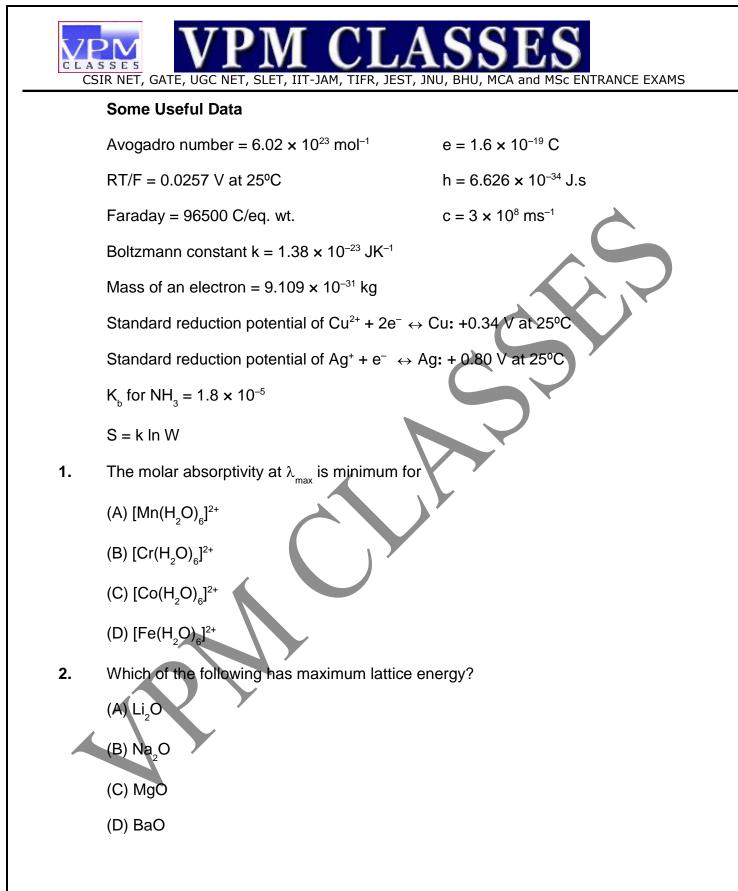
Web Site www.vpmdasses.com E-mail-vpmdasses@yahoo.com

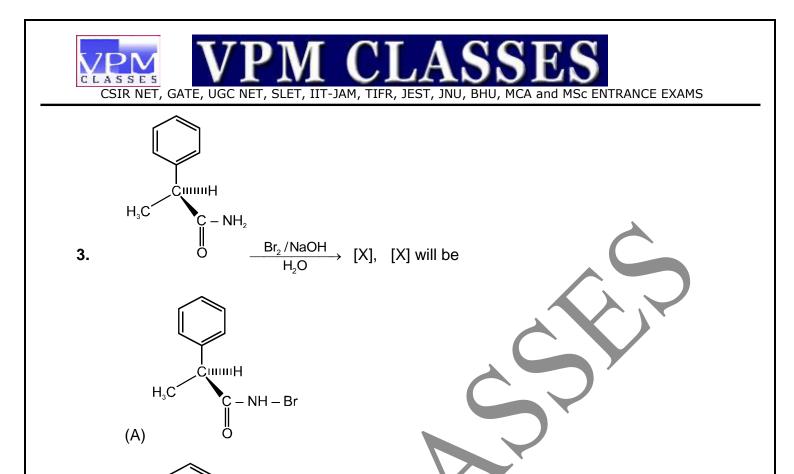
WhatsApp: 9001894070

#### Mobile: 9001297111, 9829567114

Website: <u>www.vpmclasses.com</u>

E-Mail: info@vpmclasses.com







H

H<sup>uuuu</sup>C

H<sub>3</sub>C

(B)

(C)

(D)

CH<sub>3</sub>

NH<sub>2</sub>

l <u>C</u>umuH

- CH₃

Ĥ

– CHO

NH<sub>2</sub>

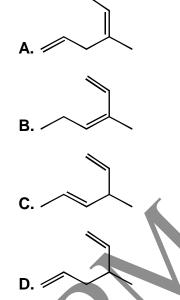
#### Mobile: 9001297111, 9829567114

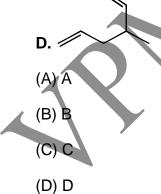
E-Mail: info@vpmclasses.com

- **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

ASSES

- (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





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

WhatsApp: 9001894070 Website: <u>www.vpmclasses.com</u>

E-Mail: <u>info@vpmclasses.com</u>





 $k_2 = 3.80 \times 10^{-5} \text{ s}^{-1}$  $\mathbf{k}_{2}$ 

The mol percent of B in the products is

(A) 23-17

k₁

- (B) 76-83
- (C) 30-16
- (D) 69-84
- Half life of the reaction is independent of initial concentration of  $H_2O_2$ . Volume of  $O_2$ 7. gas after 20 minutes is 5L at 1 atm and 27°C and after completion of the reaction 50L. The rate constant is: -
  - (A)  $\frac{1}{20}$  log10 min<sup>-1</sup>
  - (B)  $\frac{2.303}{20}$  log10 min<sup>-1</sup>
  - (C)  $\frac{2.303}{20} \log \frac{50}{45} \min^{-1}$
  - (D)  $\frac{2.303}{20} \log \frac{45}{50} \min^{-1}$
- Chromium metal can be electrolytically plated out from an acidic solution containing 8. CrO<sub>3</sub>. Assuming that all of the CrO<sub>3</sub> 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) 20,500 coul
  - (B) 41,000 coul
  - (C) 10,250 coul
  - (D) 61,500 coul

WhatsApp: 9001894070

- **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<sub>3</sub>CH<sub>2</sub>OH
  - (B) CH<sub>3</sub>OCH<sub>3</sub>
  - (C) CH<sub>3</sub>CHO
  - (D) Both A & B
- 10. The following molecule has a

(A) Centre of symmetry

HC

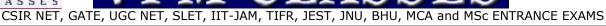
ÓН

- (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:

ÇO<sub>2</sub>H

OH

- (A) 0.01 M  $H_2S < 0.01$  M  $H_2SO_4 < 0.01$  M NaCl < 0.01 M NaNO<sub>2</sub>
- (B) 0.01 M NaCl < 0.01 M NaNO<sub>2</sub> < 0.01 M H<sub>2</sub>S < 0.01 M H<sub>2</sub>SO<sub>4</sub>
- (C) 0.01 M NaNO<sub>2</sub> < 0.01 M NaCl < 0.01 M H<sub>2</sub>S < 0.01 M H<sub>2</sub>SO<sub>4</sub>
- (D) 0.01 M H2S < 0.01 M NaNO<sub>2</sub> < 0.01 M NaCl < 0.01 M H<sub>2</sub>SO<sub>4</sub>



12. Which statement/relationship is correct?

(A) Upon hydrolysis salt of a strong base and weak acid gives a solution with pH < 7

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

- (C) Only at 25°C the pH of water is 7
- (D) The value of  $\text{pK}_{_{\rm w}}$  at 25°C is 7
- **13.** If the ionic strength of Cd  $(NO_3)_2 = 1$  unit, then the molality of Cd $(NO_3)_2$  solution will be.
  - (A) 1 unit
  - (B) 1/2 unit
  - (C) 1/3 unit
  - (D) 1/4 unit
- 14. Electrolysis of a solution of  $HSO_4^-$  ions produces  $S_2O_8^{--}$ . Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole of  $S_2O_8^{--}$  per hour
  - (A) + 71.5 amp
  - (B) 35.7 amp
  - (C) 142-96 amp
  - (D) 285-93 amp
- **15**. 2e<sup>-</sup>, standard oxidation potential = -1.09 volt. For Fe  $\longrightarrow$  Fe<sup>2+</sup> + 2e<sup>-</sup>,

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

(A)  $Br_2 + 2l^- \longrightarrow 2Br^- + l_2$ 



- (B) Fe +  $Br_2 \longrightarrow Fe^{2+} + 2Br^-$
- (C) Fe +  $I_2 \longrightarrow Fe^{2+} + 2I^-$
- (D)  $I_2 + 2Br^- \longrightarrow 2I^- + Br_2$
- Consider the following statements about intermolecular /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 Ca  $(HCO_3)_2$  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<sub>3</sub> per 10<sup>6</sup> 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 Mg  $(NH_4) PO_4$  is heated is
  - (A) Mg  $(NH_4)_2 PO_4$
  - (B) MgO
  - (C) PbO
  - (D)  $Mg_2P_2O_7$

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 Bi  $(NO_3)_3$  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<sub>2</sub>
  - (B) Kl<sub>3</sub>
  - (C) Bi (OH)<sub>2</sub>

WhatsApp: 9001894070

Website: <u>www.vpmclasses.com</u>

(D) Bi (OH)(NO<sub>3</sub>)<sub>2</sub>

- **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 HCI 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<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O
- (B)  $Na_{2}S_{2}O_{3}$ .  $5H_{2}O$
- (C)  $Na_{2}SO_{4}.10H_{2}O$
- (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) LICI > NaCl > KCl
    - (B) KCI > NaCl > LiCl
    - (C) NaCl > KCl > LiCl
    - (D) LiCl > KCl > NaCl

WhatsApp: 9001894070

E-Mail: info@vpmclasses.com

- 25. Identify the least stable ion amongst the following
  - (A) Li<sup>+</sup>

SSES

- (B) Be-
- (C) B<sup>-</sup>
- (D) C<sup>-</sup>
- 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  $(C_7H_7^+)$

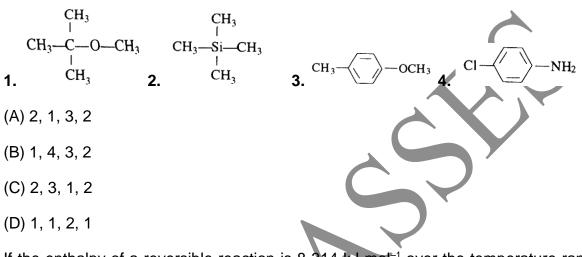
# WhatsApp: 9001894070

Website: <u>www.vpmclasses.com</u>

(D)  $C_5 H_5^+$ 

ASSES

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



- **30.** If the enthalpy of a reversible reaction is 8.314 kJ mol<sup>-1</sup> 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:-

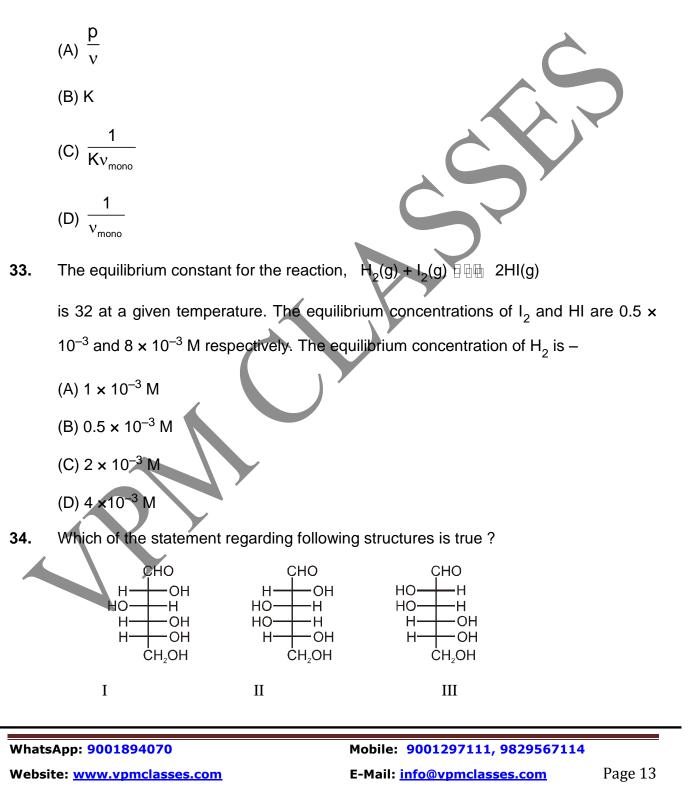
(A) 14 – pOH (B) Kw/pOH

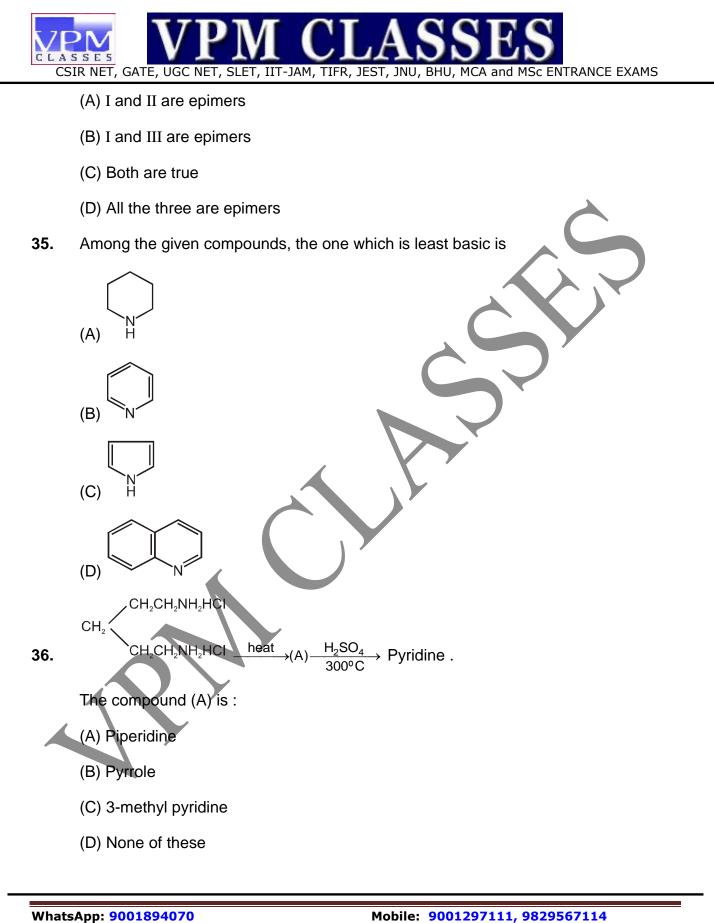
(C) 10<sup>-pOH</sup>

(D) 10<sup>-(14 - pOH)</sup>

SSES

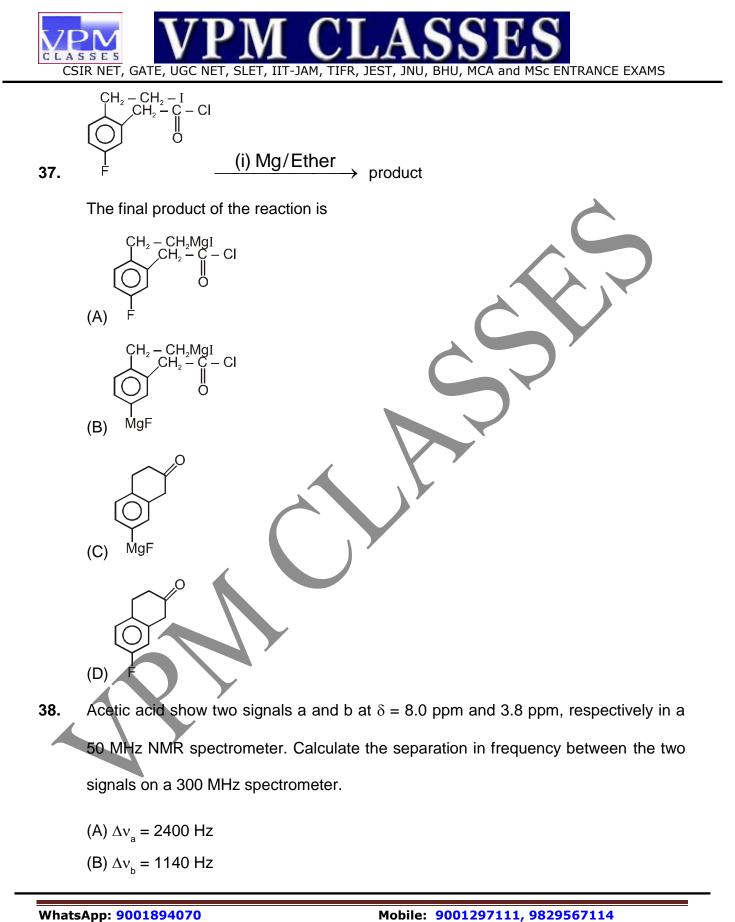
32. If v is the volume of a gas adsorbed on the surface of a solid, the plot of p/v versus p where p is the gas pressure in the langmuir adsorption isotherm, gives a straight line with slope equal to





Website: <u>www.vpmclasses.com</u>

Page 14

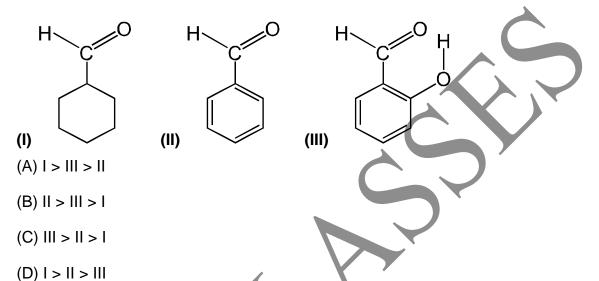




(C) A & B both

(D)  $\Delta v_a = 2400 \text{ MHz} \& \Delta v_b = 1140 \text{ MHz}$ 

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



- **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**

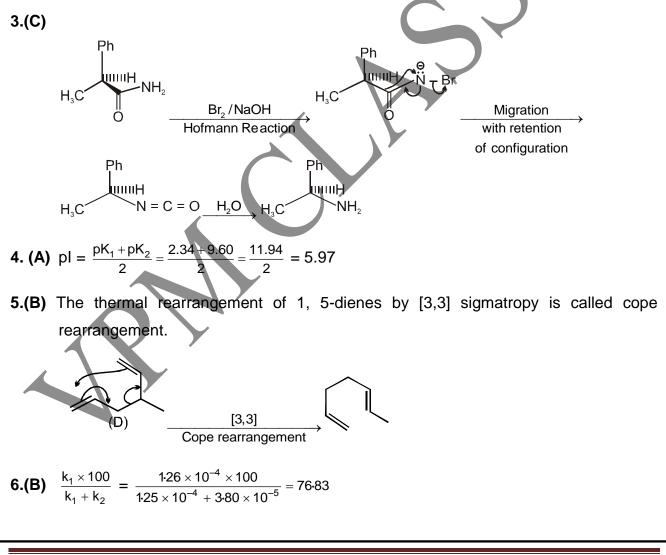
Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Answer	Α	С	С	Α	В	В	С	В	Α	В	С	С	С	Α	D	С	В	В	D	Α
Question	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Answer	В	В	D	В	В	В	С	В	Α	D	D	D	D	С	С	Α	D	С	D	В

# HINTS AND SOLUTION

**1.(A)**  $[Mn(H_2O)_6]^{2+} = Mn^{+2} = 3d^5$ 

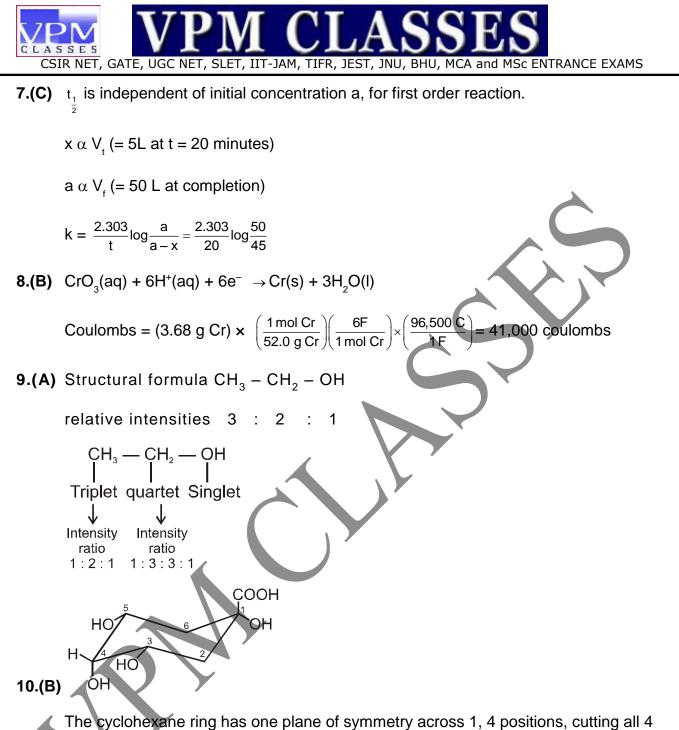
In  $[Mn(H_2O)_6]^{2+}$  complex all transitions are not only laporte forbidden but also spin forbidden. Absorptions associated with doubly forbidden transitions are extremely weak with extinction coefficients several times smaller than those for singly forbidden transitions. So the molar absorptivity at  $\lambda_{max}$  is minimum for  $[Mn(H_2O)_6]^{2+}$ .

2.(C) MgO, Mg<sup>2+</sup> ion is smallest in size and double the charge in comparison to Li<sup>+</sup> and Na<sup>+</sup> ions.



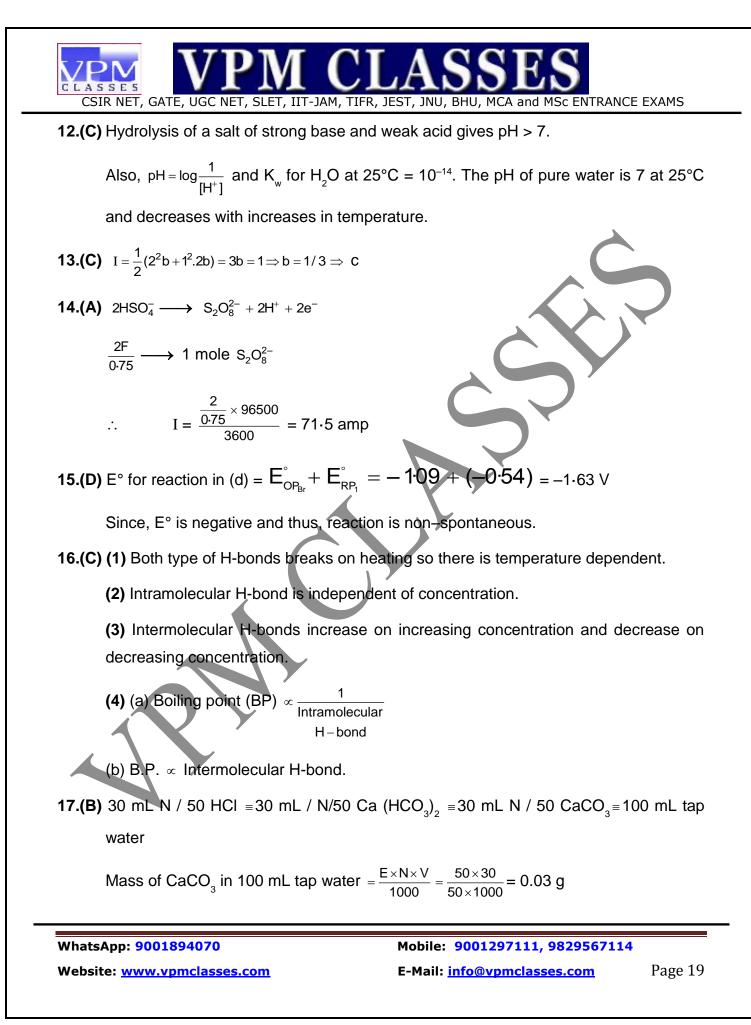
#### WhatsApp: 9001894070

Mobile: 9001297111, 9829567114



- 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 pH< 7. NaNO<sub>2</sub> on hydrolysis gives alkaline solution of pH > 7. NaCl is neutral and  $H_2S$  is weak acid.

WhatsApp: 9001894070 Website: <u>www.vpmclasses.com</u>





 $\Rightarrow$  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)** 
$$2Mg(NH_4)PO_4 \xrightarrow{O} Mg_2P_2O_7 + H_2O + 2NH_3$$

- 20.(A) Both lattice energy and hydrolysis energy decreases moving down the group due to gradual increase in size of M<sup>++</sup> 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 (NO<sub>3</sub>)<sub>3</sub> undergoes hydrolysis. Nitric acid is formed. Which oxidises KI to iodine. The liberated iodine dissolves in KI to form yellow solution of KI<sub>3</sub>.

$$Bi(NO_3)_3 + H_2O \longrightarrow [Bi(OH)(NO_3)_2] + HNO_3; 2HNO_3 \longrightarrow H_2O + 2NO_2 + O_3 \longrightarrow H_2O + 2NO_2 + O_3; 2HNO_3 \longrightarrow H_2O + 2NO_2 + O_3 \longrightarrow H_2O + 2NO_2 \longrightarrow H$$

$$2KI + H_2O + O \longrightarrow 2KOH + I_2 ; I_2 + KI \longrightarrow KI_3$$
  
Darkbrown;  $I_2 + KI \longrightarrow Yellow solution$ 

**22.(B)**  $X = Na_2S_2O_3.5H_2O_3$ 

$$Na_{2}S_{2}O_{3} + 2HCI \longrightarrow 2NaCI + H_{2}O + S + SO_{2}$$

$$\mathsf{KI}_3 + 2\mathsf{Na}_2\mathsf{S}_2\mathsf{O}_3 \longrightarrow \mathsf{KI} + 2\mathsf{Na}_1 + \mathsf{Na}_2\mathsf{S}_4\mathsf{O}_6$$

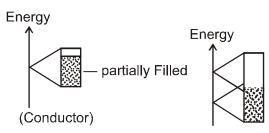
$$2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S + H_2SO_4$$

- **23.(D)**  $2AgBr + 4Na_2S_2O_3 \rightarrow 2Na_3[Ag(S_2O_3)_2] + 2NaBr$
- **24.(B)** The ease of ionization of the given compounds will be in the order LiCl < NaCl < KCl, hence equivalent conductance at infinite dilution in the same order.

WhatsApp: 9001894070 Website: <u>www.vpmclasses.com</u>

- 25.(B) Be<sup>-</sup> is attaining 2s<sup>2</sup>2sp<sup>1</sup> configuration by losing its fulfilled stability of 2s<sup>2</sup> 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<sup>8</sup> 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  $C_6H_5C_2H_5$  (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 trophylium ion.

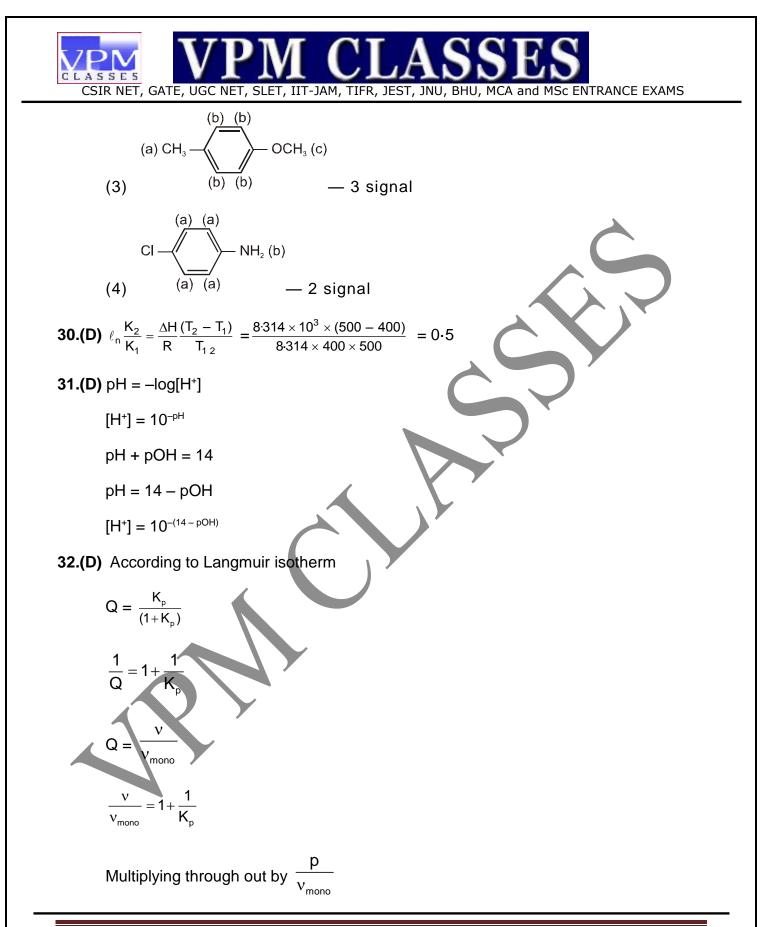
**29.(A)** (1) (a) 
$$CH_{3}(a)$$
 (b)  
(a)  $CH_{3} - C - OCH_{3}(b)$   
(b) (c)  $CH_{3}$  (c

(a) 
$$CH_3$$
  
(a)  $CH_3 - Si - CH_3$  (a)  
(2) (a)  $CH_3$  — 1 signal

WhatsApp: 9001894070

### Mobile: 9001297111, 9829567114

E-Mail: info@vpmclasses.com

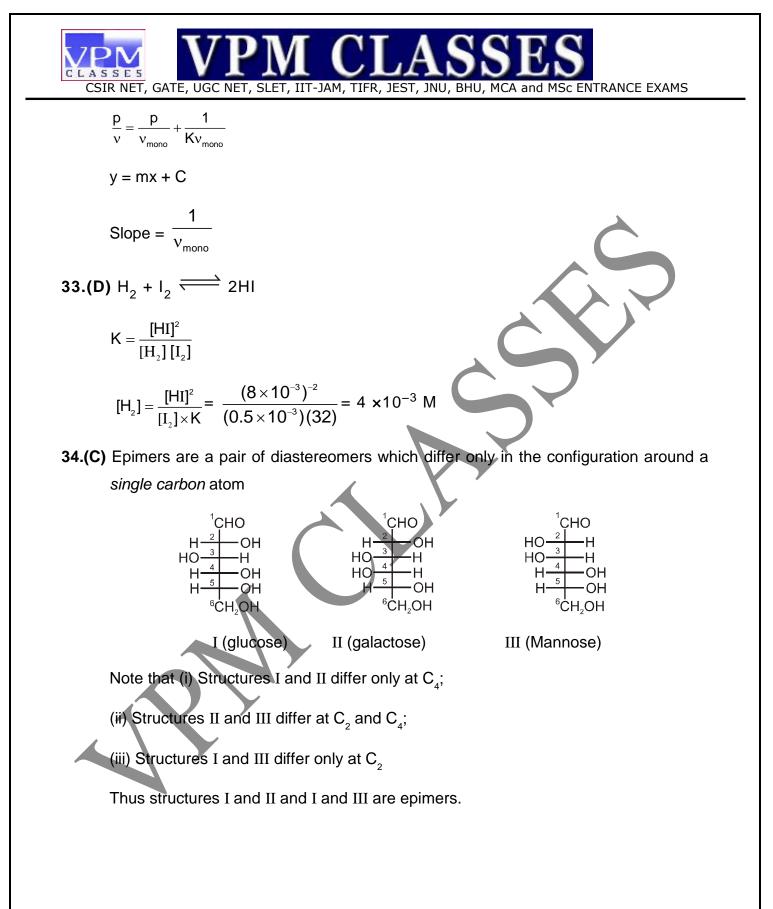


WhatsApp: 9001894070

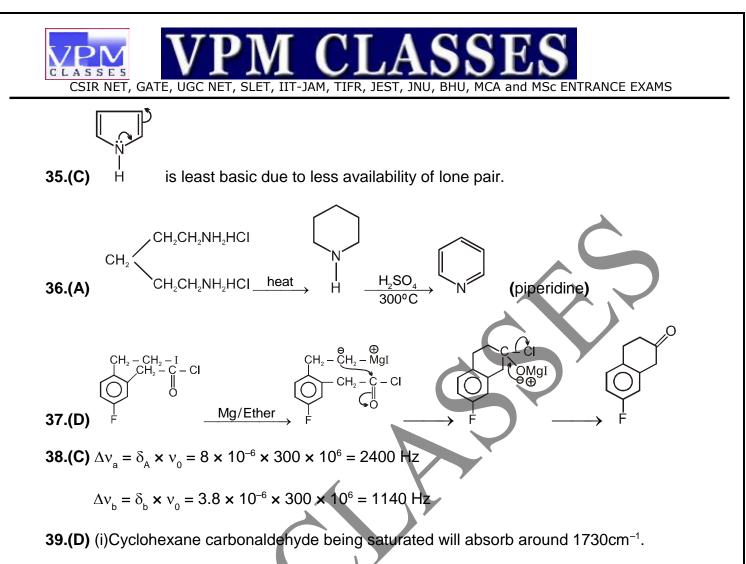
### Mobile: 9001297111, 9829567114

Website: <u>www.vpmclasses.com</u>

E-Mail: info@vpmclasses.com



WhatsApp: 9001894070 Website: <u>www.vpmclasses.com</u>



(ii) In benzaldehyde the absorption will be shifted to lower frequency (1700 cm<sup>-1</sup>) due to conjugation.

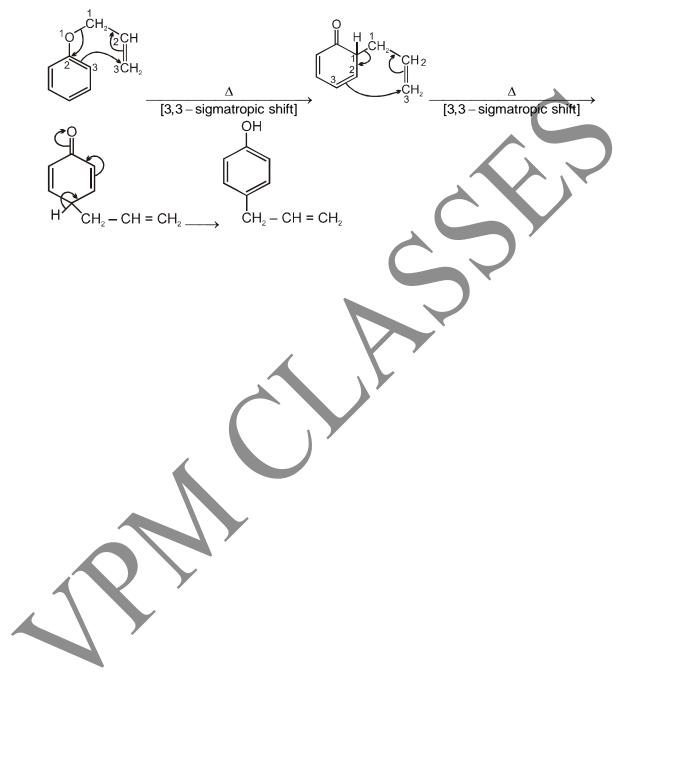
(iii) In salicylaldehyde the internal (chelate) hydrogen bonding causes a further large frequency shift to around 1666 cm<sup>-1</sup>.



# VPM CLASSES

CSIR NET, GATE, UGC NET, SLET, IIT-JAM, TIFR, JEST, JNU, BHU, MCA and MSc ENTRANCE EXAMS

40.(B)



WhatsApp: 9001894070

Website: <u>www.vpmclasses.com</u>

## Mobile: 9001297111, 9829567114

E-Mail: info@vpmclasses.com

Page 25