IIT JAM

CHEMISTRY
SOLVED SAMPLE PAPER

* DETAILED SOLUTIONS
* PROJECTED IIT JAM RANK

IIT JAM-CY   CHEMISTRY   (FMTP)

Attempt ALL the 60 questions.

There are a total of 60 questions carrying 100 marks.

Section-A contains a total of 30 **Multiple Choice Questions (MCQ).** Q.1 - Q.10 carry 1 mark each and Questi ons Q.11 - Q.30 carry 2 marks each.

Section-B contains a total of 10 **Multiple Select Questions (MSQ).** Questions Q.31 - Q.40 belong to this section and carry 2 marks each with a total of 20 marks.

Section-C contains a total of 20 **Numerical Answer Type (NAT)** questions. Questions Q.41 - Q.60 belong to this section and carry a total of 30 marks. Q.41 - Q.50 carry 1 mark each and Questions Q.51 - Q.60 carry 2 marks each.

In **Section-A** for all 1 mark questions, 1/3 marks will be deducted for each wrong answer. For all 2 marks questions, 2/3 marks will be deducted for each wrong answer. In **Section-B** (MSQ), there is **NO NEGATIVE** and **NO PARTIAL** marking provisions. There is **NO NEGATIVE** marking in **Section-C** (NAT) as well.

**Time : 3 Hours   MAX.MARKS : 100   MARKS SCORED : ☐**

SECTION-A (QUESTIONS-1-30) MULTIPLE CHOICE QUESIONS (MCQs)

1. Which of the following is an oxidizing agent?

(A) $Mn(CO)_5$ (B) $Fe(CO)_5$ (C) $Mn_2(CO)_{10}$ (D) $Fe_2(CO)_9$

2. The species having bond order different from that in CO is

(A) NO^- (B) NO^+ (C) CN^- (D) N_2

3. $(Me)_2SiCl_2$ on hydrolysis will produce

(A) $(Me)_2Si(OH)_2$ (B) $(Me)_2Si = O$

(C) $- [- O - (Me)_2Si - O -]_n -$ (D) $Me_2SiCl(OH)$

4. The correct matching is

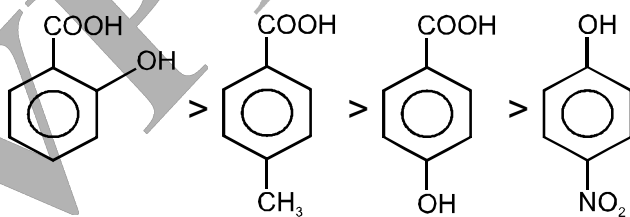| **Phenols**	**pK$_a$**
(i)	(4)

(ii)

(7)

(iii)

(10)

(iv)

(9)
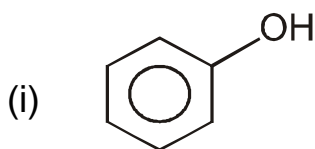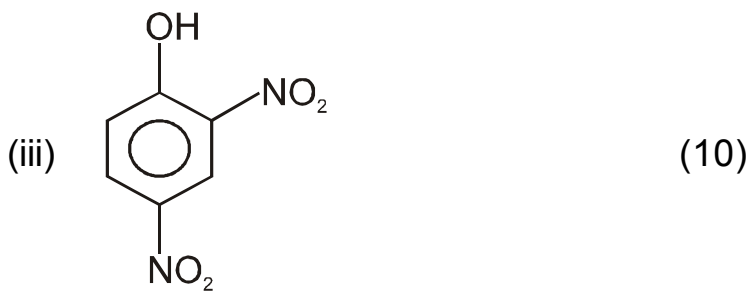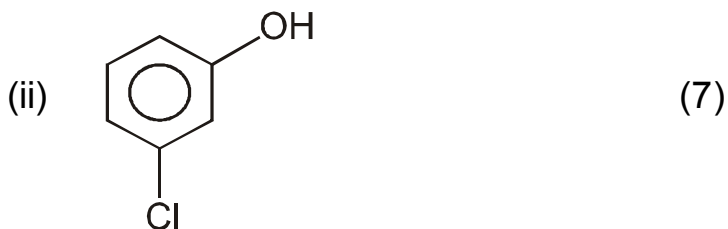
(A) i-(9), ii-(7), iii-(4), iv-(10) (B) i-(9), ii-(10), iii-(7), iv-(4)

(C) i-(10), ii-(9), iii-(4), iv-(7) (D) i-(10), ii-(7), iii-(4), iv-(9)

5. Two forms of D-glucopyranose, are called.

(A) Enantiomers (B) Anomers (C) Epimers (D) Diastereomers

6. Among the following compounds, the most acidic is

(A) p-nitrophenol   (B) p-hydroxybenzoic acid
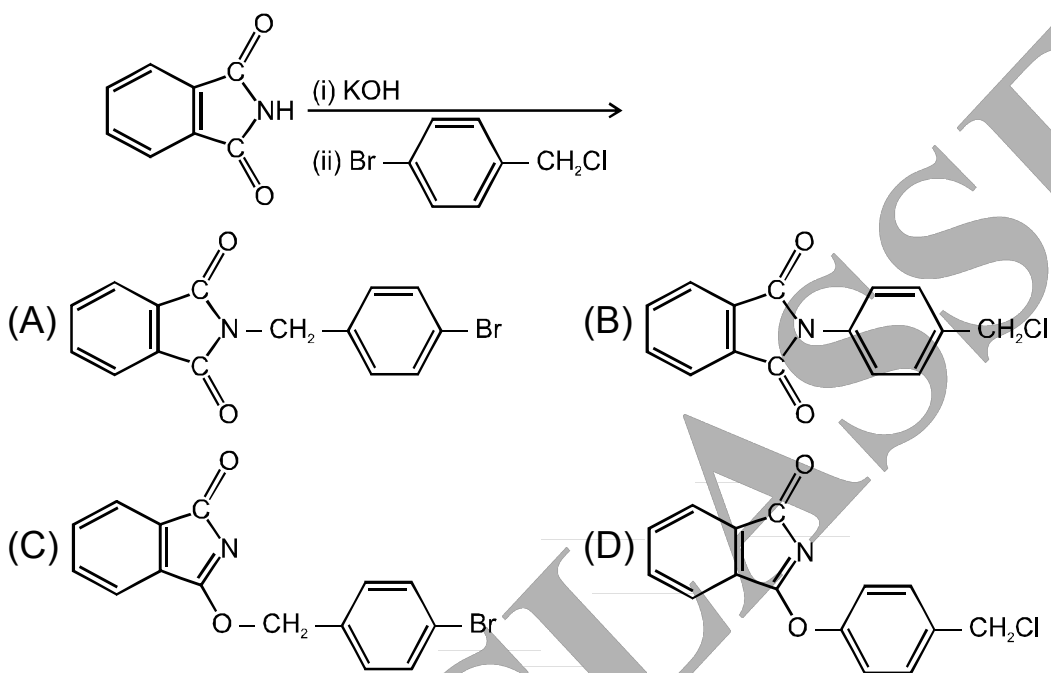
(C) o-hydroxybenzoic acid   (D) p-toluic acid

7. If 'a' is the edge length of the unit cell of an atomic crystal having face centred cubic lattice. Then what is the distance of closet approach between the two atoms in the crystal ?

(A) $\frac{1}{2}(\sqrt{2a})$ (B) $\frac{1}{2}(\sqrt{4a})$ (C) $\frac{1}{4}(\sqrt{2a})$ (D) $2\sqrt{2a}$

**8.** The value of compression factor (Z) for the gas represented by an equation

$P = \dfrac{nRT}{V - nb}$; if V_m (molar volume) = 11b then Z will be:

(A) 1.1   (B) 1.2   (C) 1.4   (D) 1.6

9. The temperature of 54 g of water is raised from 15ºC to 75ºC at constant pressure. The change in the enthalpy of the system (given that $C_{p.m}$ of water = 75 JK⁻¹ mol⁻¹) is

(A) 4.5 kJ   (B) 13.5 kJ   (C) 9.0 kJ   (D) 18.0 kJ

10. For the reaction :
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$,
at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by
(A) adding a suitable catalyst
(B) adding an inert gas
(C) decreasing the volume of the container
(D) increasing the amount of CO(g)

11. The percentage transmittance of an aqueous solution of disodium fumarate at 250 nm and 25ºC in 19.2% for a 5×10^{-4} mol L⁻¹ solution in a 1 cm cell. The molar absorption coefficient, ε is

(A) 1.43×10^5 L mol⁻¹ cm⁻¹   (B) 1.42×10^{-5} L mol⁻¹ cm⁻¹

(C) 1.43×10^{-3} L mol⁻¹ cm⁻¹   (D) 1.43×10^3 L mol⁻¹ cm⁻¹

12. What is crystal field splitting for cube (Δ_{cubic})?

(A) $\dfrac{4}{9}\Delta_t$ (B) $\dfrac{8}{9}\Delta_0$ (C) $\dfrac{\Delta_t}{2}$ (D) $\dfrac{4}{9}\Delta_0$

13. For the term symbol ^3D the value of J will be $\rightarrow$

(A) $^3D_{\frac{1}{2}}$ (B) $^3D_1\,^3D_2\,^3D_3$ (C) $^3D_{\frac{1}{2}},\,^3D_{\frac{3}{2}}$ (D) $^3D_0$

14. The correct shape of $[TeF_5]^-$ ion on the basis of VSEPR theory is
(A) Trigonal bipyramidal   (B) Square pyramidal
(C) Pentagonal planar   (D) See-saw

15. The numbers of P-S and P-P bonds in the compound P_4S_3 are, respectively,

(A) 6 and 3   (B) 4 and 3   (C) 3 and 6   (D) 6 and 2

16. The complex that shows orbital contribution to the magnetic moment, is

(A) $[Cu(H_2O)_6]^{2+}$ (B) $[Ni(H_2O)_6]^{2+}$ (C) $[Co(H_2O)_6]^{2+}$ (D) $[Cr(H_2O)_6]^{2+}$

17. The major product of the following reaction is

18. The major product formed in the following reaction is

(C)

(D)

19. $\xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) NaOH}/100^\circ C}$ Major Product is :

(A)

(B)

(C)

(D)
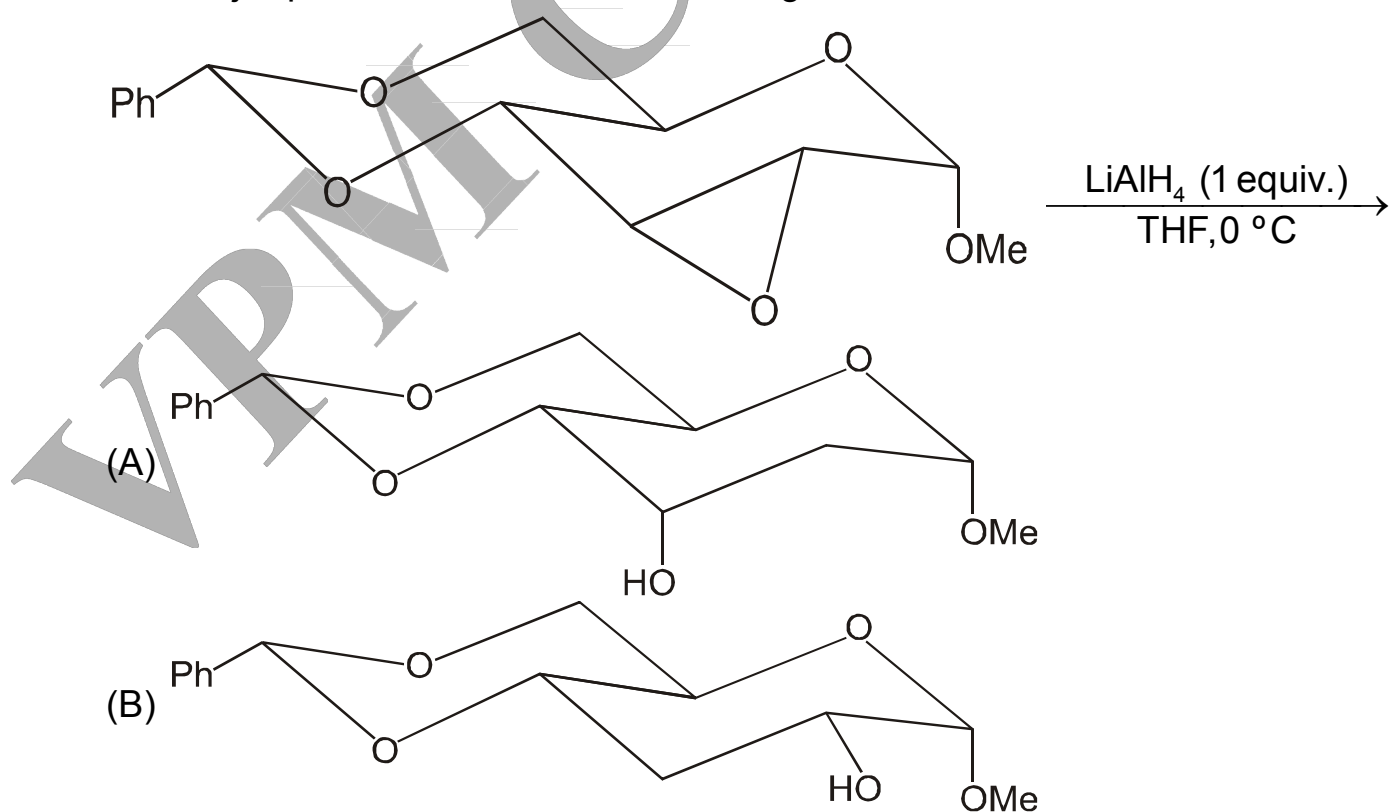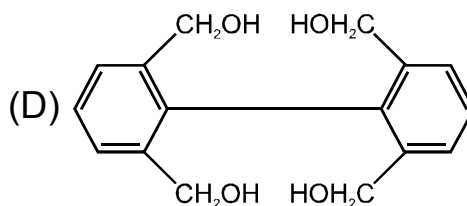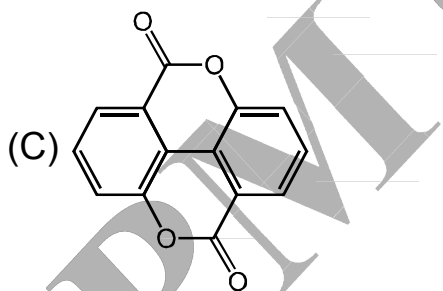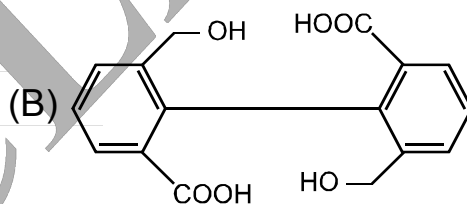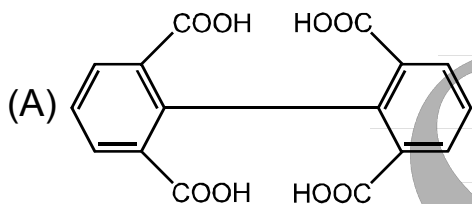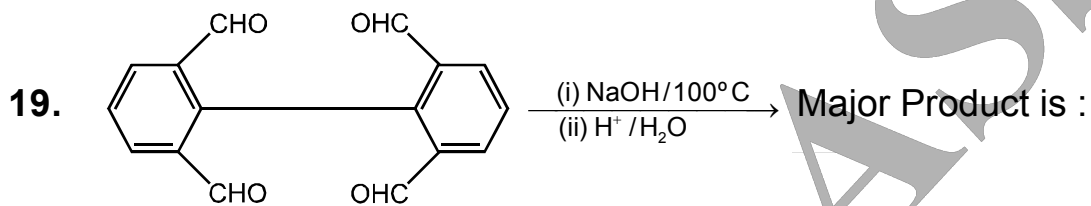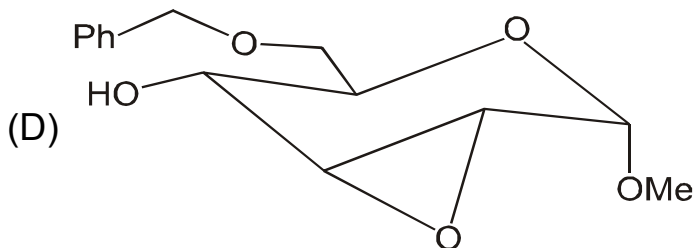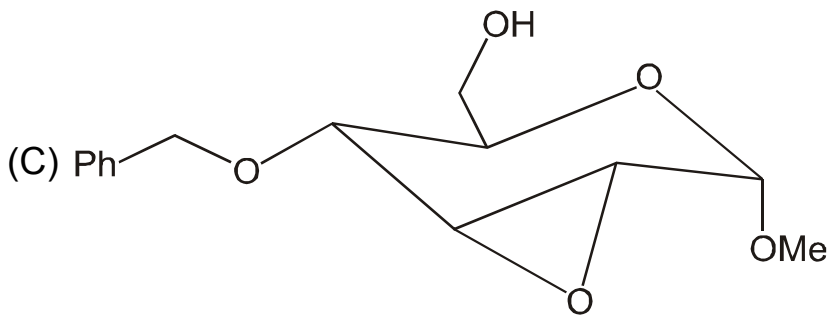
20. At pH 10, tryptophan exists as

(A)

(B)

(C)

(D)
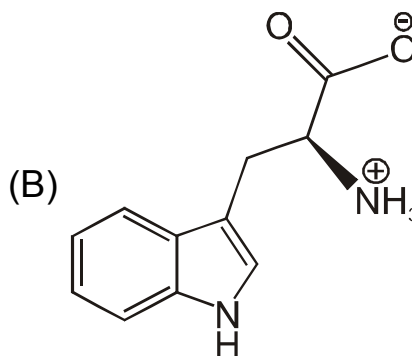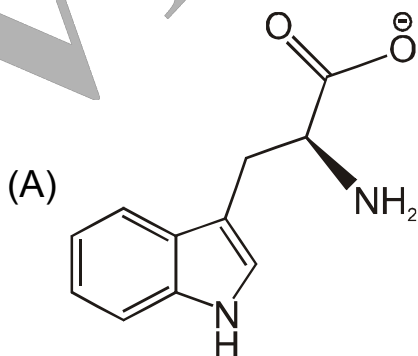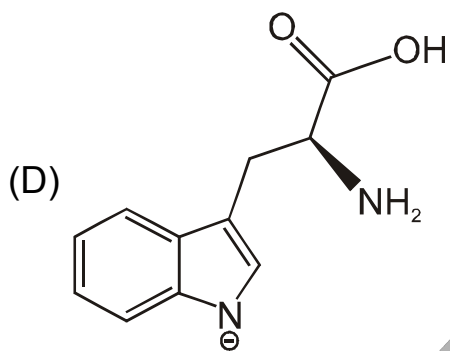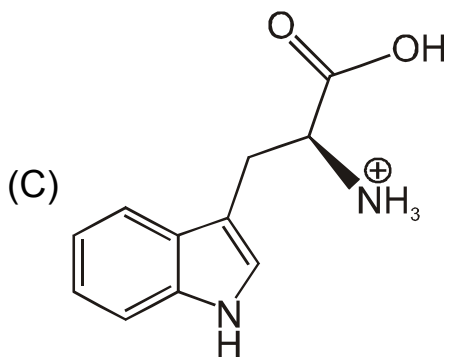
21. The major product formed in the following reaction sequence is

(i) $HOCH_2CH_2OH$, TsOH

(ii) Cp_2Ti — Cl

(iii) H_3O^+

(A)

(B)

(C)

(D)
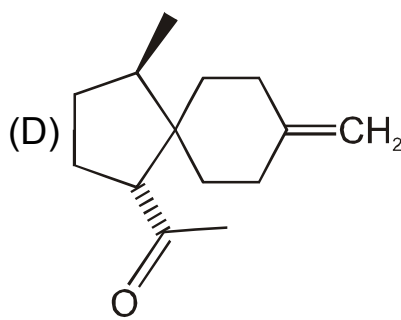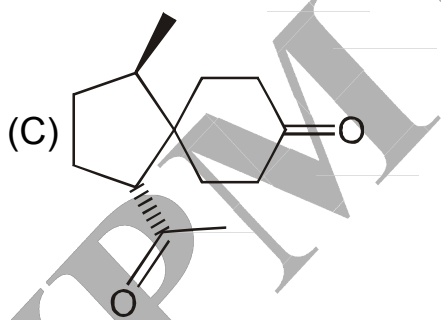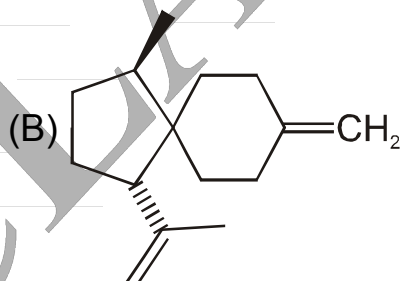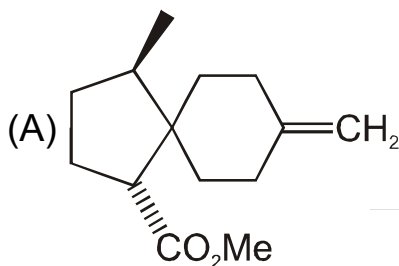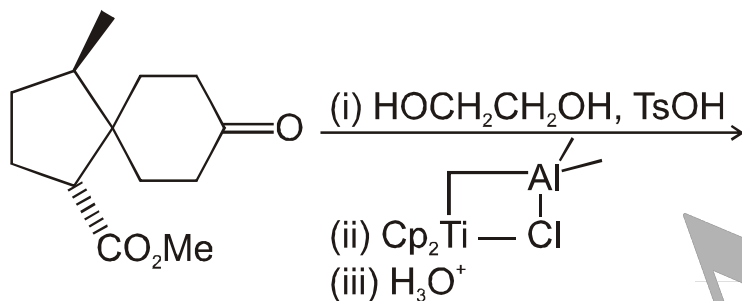
22. In the UV-visible absorption spectrum of an α, β-unsaturated carbonyl compound, with increasing solvent polarity,

(A) n-π^* transitions undergo hypsochromic shift, π-π^* undergo bathochromic shift

(B) n-π^* transitions undergo bathochromic shift, π-π^* undergo hypsochromic shift

(C) both n-π* and π-π* transitions undergo bathochromic shift

(D) both n-π* and π-π* transitions undergo hypsochromic shift

23. $AgNO_3$(aq.) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is

(P)

Λ

volume

(Q)

Λ

volume

(R)

Λ

volume

(S)

Λ

volume
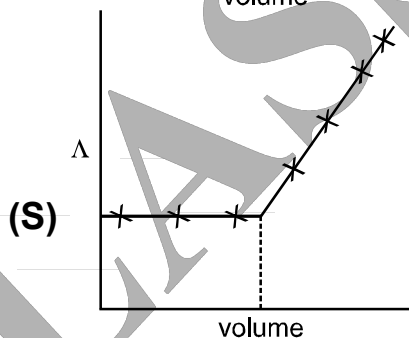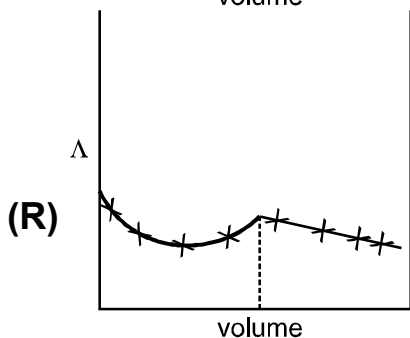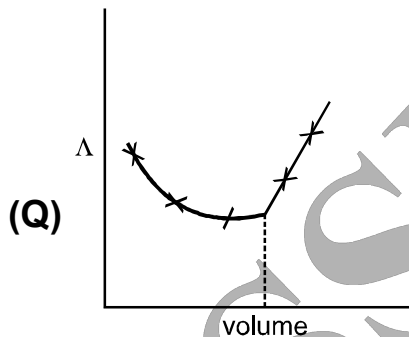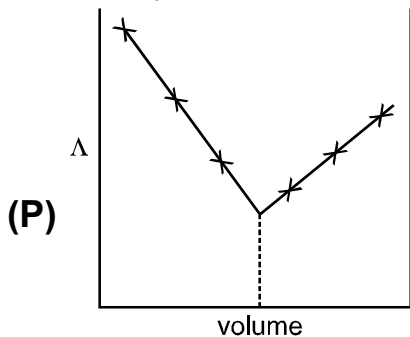
(A) (P)　　　　　(B) (Q)　　　　　(C) (R)　　　　　(D) (S)

24. A partially dried clay mineral contains 8% water. The original sample contained 12% water and 45% silica. The % of silica in partially dried sample is —

(A) 50%　　　　(B) 49%　　　　(C) 55%　　　　(D) 47%

25. For the molecule HCl, the harmonic frequency ω_e = 2330 cm^{-1} and anharmonic constant is 56 cm^{-1}. Calculate the energy of first two vibrational levels and determine the spacing between them.

(A) 1015 cm^{-1}, 3215 cm^{-1}, 2200 cm^{-1}　　(B) 1151 cm^{-1}, 3425 cm^{-1}, 2274 cm^{-1}

(C) 1099 cm^{-1}, 3325 cm^{-1}, 2226 cm^{-1}　　(D) 1105 cm^{-1}, 3399 cm^{-1}, 2294 cm^{-1}

26. Consider the following reaction of methane with molecular chlorine —

$$CH_{4(g)} + Cl_{2(g)} \rightarrow CH_3Cl_{(g)} + HCl_{(g)}$$
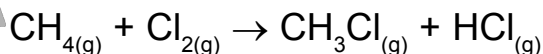
The mechanism of this reaction is —

$$Cl_2 \xrightarrow{K_1} 2Cl^\bullet$$

$$Cl^\bullet + CH_4 \xrightarrow{K_2} HCl + CH_3^\bullet$$

$$CH_3{}^{\bullet} + Cl_2 \xrightarrow{K_3} CH_3Cl + Cl^{\bullet}$$

$$Cl^{\bullet} + Cl^{\bullet} \xrightarrow{K_4} Cl_2$$
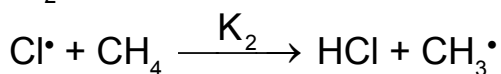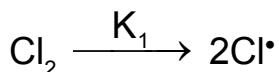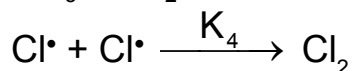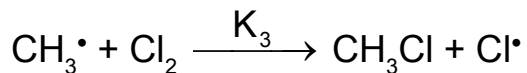
The rate law of this reaction is —

(A) $R = K_2\left(\dfrac{K_1}{K_4}\right)^{1/2}[CH_4][Cl_2]^{1/2}$

(B) $R = \dfrac{K_1K_2}{K_4}[CH_4][Cl_2]^{1/2}$

(C) $R = K_2\left(\dfrac{K_1}{K_4}\right)^{1/2}[CH_4]^{1/2}[Cl_2]^{1/2}$

(D) $R = \dfrac{K_1K_2}{K_4}[CH_4]^{1/2}[Cl_2]^{1/2}$

27. The dissociation constant of aniline, acetic acid and water at 25ºC are 3.83×10^{-10}, 1.75×10^{-5} and 1.008×10^{-14}. The percentage hydrolysis of aniline acetate in a decimolar solution is —

(A) 17.43   (B) 29.25   (C) 54.95   (D) 66.17

28. A molecule has a ground state and two excited electronic energy levels, all of which are nondegenerate with the energies : $E_0 = 0$, $E_1 = 1 \times 10^{-20}$ J and $E_2 = 3 \times 10^{-20}$ J. If P_0, P_1 and P_3 are fractions of molecules occupied in ground, first and second excited states, respectively, at 298K, then, $P_0 : P_1 : P_2 = ?$

(A) 0.919 : 0.081 : 0.001   (B) 0.900 : 0.098 : 0.002

(C) 0.666 : 0.333 : 0.111   (D) 0.880 : 0.088 : 0.022**8.**

29. While carrying out the titration of a weak acid with a strong base, the pH of the solution is measured as a function of the added titrant. The result is shown below.
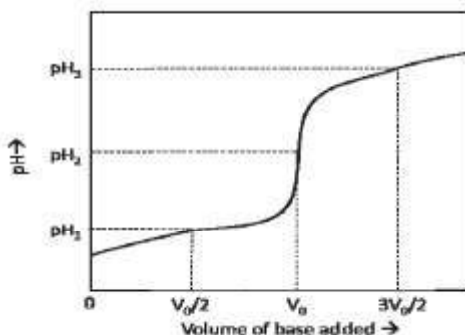
Three pH values have been marked, corresponding to 3 different volumes of the added base. V_0 corresponds to the 'end point' or the 'stoichiometric point' of neutralization. What is the pKa of the acid?

(A) pH_1 (B) pH_2

(C) pH_3 (D) intermediate of pH_2 & pH_3

30. Consider the following sequential reaction scheme :-

$$A \xrightarrow{K_A} I \xrightarrow{K_I} p$$
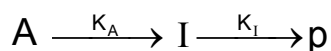
Assuming that only reactant A is present at t = 0 , what is the expected time dependence of [p] using steady state approximate ?

(A) $[p] = [A]_o (1 + e^{-kAt})$

(B) $[p] = [A]_o [1 - e^{+kAt}]$

(C) $[p] = [A]_o [1 - e^{-KAt}]$

(D) $[p] = [A]_o [1 + e^{+kAt}]$

SECTION-B (QUESTIONS-31-40)MULTIPLE SELECT QUESTIONS (MSQs)

31. The correct statements about the reaction of X and Y with $NaNH_2$ are :

(X) Ph, Ph, Ph, Ph, H (tetraphenylmethane structure)

(Y) Ph, Ph, Ph, H (triphenylcyclopropene structure)
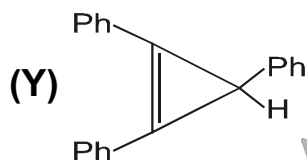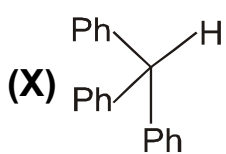
(A) X reacts faster than Y

(B) Y reacts faster than X

(C) X and Y behave as Lewis acis

(D) X is stronger Bronsted acid than Y

32. The correct statements about conformations X and Y of 2-butanone are

(X) H_3C, H, H, O, CH_3 (Newman projection)

(Y) H, H, H_3C, O, CH_3 (Newman projection)
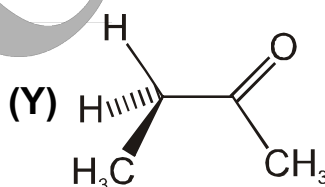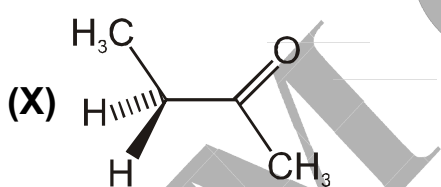
(A) X is more stable than Y

(B) Y is more stable than X

(C) Methyl groups in X are *anti*

(D) Methyl groups in Y are *gauche*

33. Select the options with correct orders regarding IR frequencies.

(A) (I) < (II) $(\nu_{C=O})$

(B) (I) < (II) $(\nu_{C=O})$

(C) (I) < (II) $(\nu_{C=O})$

(D) (I) > (II) $(\nu_{C=O})$
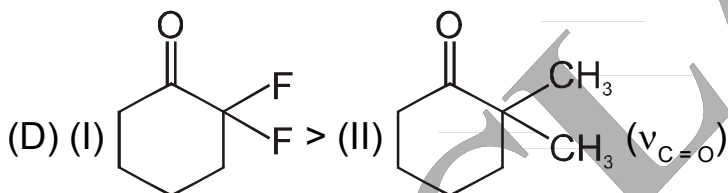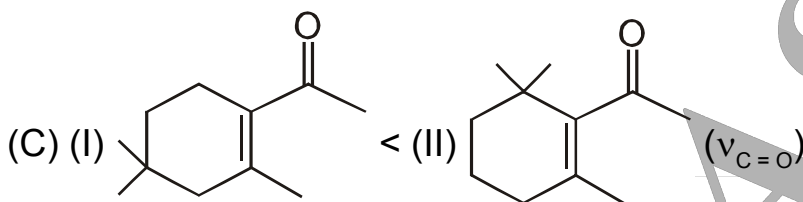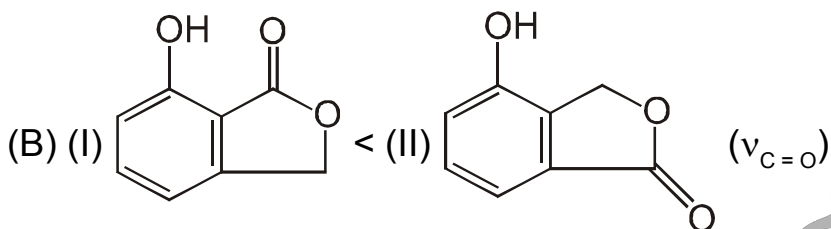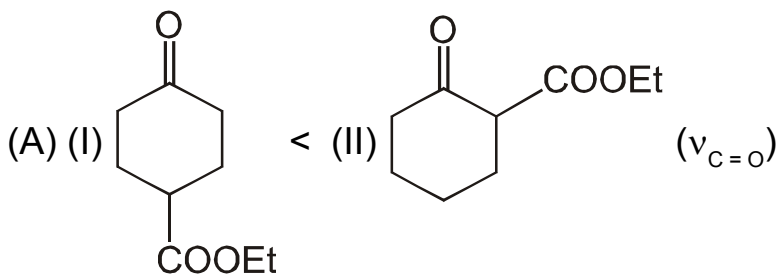
34. The correct dipole moment order are :

(A) <

(B) >

(C)
$$\begin{array}{c} CH_3 \\ \diagdown \\ CH_3 \end{array} CH - Cl < CH_2 = CH - Cl$$

(D) $HOOC \!-\! \langle \ominus | \oplus \rangle > \langle \ominus \ \oplus \rangle \!-\! COOH$
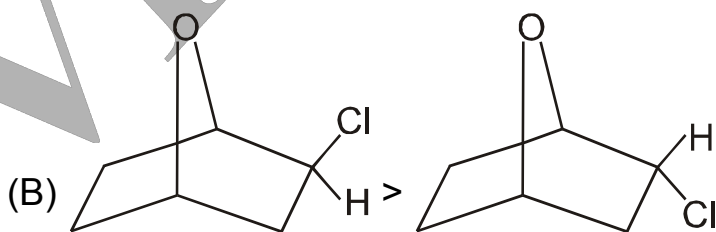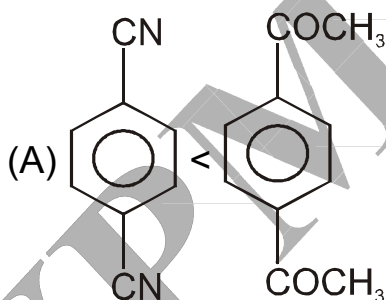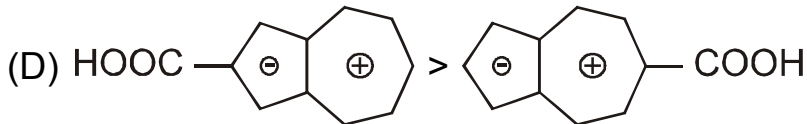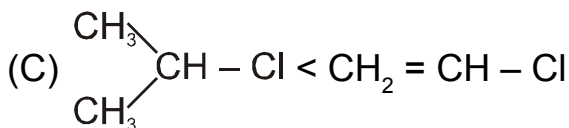
35. For H_3PO_3 and H_3PO_4 the incorrect choice is :

(A) H_3PO_3 is dibasic and reducing (B) H_3PO_3 is dibasic and non-reducing

(C) H_3PO_4 is tribasic and reducing (D) H_3PO_3 is tribasic and non-reducing

36. Which of the following compounds show optical isomerism?

(A) Cis-[co(NH_3)_4Cl_2]   (B) trans-[co(en)_2 cl_2]

(C) Cis-[Co(en)_2 Cl_2]   (D) [Co(en)_3]^{3+}
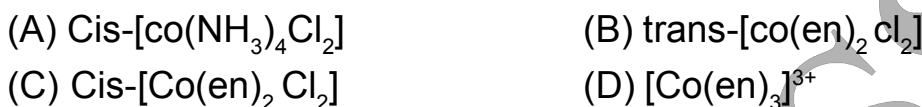
37. Which of the following are staked layer Polymers?

(A) Boron Nitride   (B) Graphite

(C)
$$\left[\begin{array}{c} R \\ | \\ Si - O \\ | \\ O \\ | \end{array} \right]_n$$
          (D) $[SiO_3]_n^{n-}$
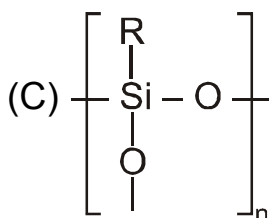
38. Which of the following solutions will not have pH close to 1.0 ?

(A) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH

(B) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH

(C) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH

(D) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH
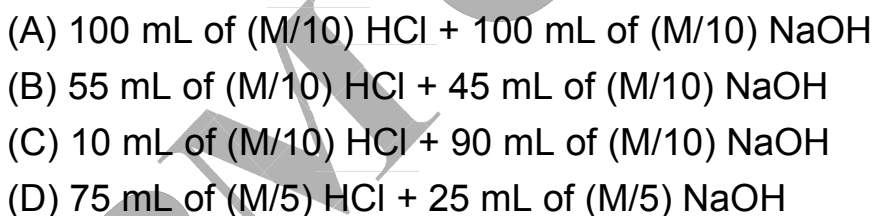
39. For the given cell, at 298 K

Pt | Q, QH_2, H^+ || 1 M KCl | Hg_2Cl_2(s) | Hg(l) | Pt

the emf will be _____ when pH = 5.0 and the pH will be _____ when E_{cell} = 0.

(A) E_{cell} = –0.1239 V   (B) E_{cell} = 0.1239 V

(C) pH = 6.1   (D) pH = 7.1

40. When an X-ray powder pattern of crystalline copper is obtained using X-rays from copper target (the wavelength of the K_α - line is 154.05 pm), reflections are found at $21.65°, 25.21°, 37.06°, 47.58°$ and other angles. The length of a side of the unit cell and the radius of copper atom will be _____ and _____

respectively.

(A) a = 363.2 pm (B) a = 264.2 pm

(C) r = 128.3 pm (D) r = 96.2 pm

SECTION-C (QUESTIONS-41-60)NUMERICAL ANSWER TYPE (NAT)

41. What is the standard enthalpy of a reaction (in kJ mol^{-1}) for which the equilibrium constant is doubled when the temperature is increased by 10 K at 298 K ?

42. A zinc rod is placed in 0.1 M solution of zinc sulphate at 25°C. Assuming that the salt is dissociated to the extent of 95 percent at this dilution, find out the potential of the electrode at this temperature (in V)?

43. For the following equation of state

$P = \dfrac{RT}{V_m} - \dfrac{B}{V_m^2} + \dfrac{C}{V_m^3}$; B and C are constants. What will be the value of critical compression factor (Z_c) ?

44. For the reaction, A + B $\rightleftharpoons$ 2C ; 2 mole of A and 3 mole of B are allowed to react. If the equilibrium constant is 4 at 400°C, what will be the mole of C at equilibrium ?

45. What is the number of lone pair(s) of electrons in $XeOF_4$?

46. How many fundamental bands are observed in the infrared spectrum of benzene?

47. The difference in the oxidation numbers of the two types of sulphur atoms in $Na_2S_4O_6$ is _____.

48. A decapeptide (Mol. Wt. 796) on complete hydrolysis gives glycine (Mol. Wt. 75), alanine and phenylalanine.

Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present

in the decapeptide is _____.

49. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is _____.

50. Total number of vibrations in allyl bromide are?

51. The total number of stereoisomers (Geometrical + Optical) possible for 1, 3-dichlorocyclohexane are ,
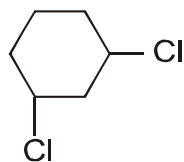
52. The transmittance of a solution having 2M concentration is 20% in a 1 mm cell. Then molar absorptivity of solution (ε) is _____.

53. The molar conductance at infinite dilution of HCl, NaCl and NaZ (Sodium Crotonate) are 425×10^{-4}, 125×10^{-4} and 80×10^{-4} Sm^2 mol^{-1}, respectively. The specific conductance of 0.001 M aqueous solution of crotonic acid (HZ) is 3.8×10^{-3} Sm^{-1}. What is the degree of dissociation ?

54. A 1000 mL sample of a gas at $-73°C$ and 2 atmosphere is heated to $123°C$ and the pressure is reduced to 0.5 atmosphere. What will be the final volume (in ml)?

55. The vapour-pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour-pressure of the solution (in mm of Hg).

56. At 518ºC, the half life for the decomposition of a sample of gaseous acetaldehyde (ethanol) initially at 363 Torr was 410s. When the pressure was 169 Torr, the half life was 880 s. Determine the order of the reaction.

57 Calculate J_{max} for a rigid diatomic molecule for which at 300 K, the rotational constant is 1.566 cm^{-1}.

58. In metal hydrides, the reference absorbs at 1200 Hz higher frequency than the metal Hydride. Calculate the chemical shift of metal Hydride at 400 MHz.

59. What is the isoelectric point of the given structure ? (pka = 5.7, pkb = 9.3)
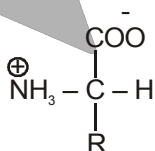
60. A monochromatic radiation is incident in a solution of .05 molar concentration of substance the intensity of radiation is reduced to $\dfrac{1}{10}$ of the initial value after passing through 20 cm length of the solution. Calculate the molar extinction coefficient (ε) of the substance (in mole liter cm^{-1}).

Ques	1	2	3	4	5	6	7	8	9	10
Ans	A	A	C	C	B	C	A	A	B	D
Ques	11	12	13	14	15	16	17	18	19	20
Ans	D	B	D	B	A	C	A	A	B	A
Ques	21	22	23	24	25	26	27	28	29	30
Ans	C	A	D	D	B	A	C	A	A	C
Ques	31	32	33	34	35	36	37	38	39	40
Ans	A,D	D	A,B,C,D	A,B,D	B,C,D	C,D	A,B	A,B,C	A,D	A,C
Ques	41	42	43	44	45	46	47	48	49	50
Ans	53	-0.79	0.3333	2.4	1	30	5	6	5	21
Ques	51	52	53	54	55	56	57	58	59	60
Ans	3	3.495	0.10	8000	65.71	2	8	13	5.2	1

HINTS & SOLUTION

1.(A) $Mn(CO)_5$ **[less stable (O.A.)]** $+ e^- \rightarrow [Mn(CO)_5]^-$ **[more stable, as EAN of Mn = 36 (Kr)]**

2.(A) The bond order of CO = 3. NO^+, CN^- and N_2 are isoelectronic with CO, have the same bond orders as CO. NO^- ($16e^-$) has bond order of 2.

3.(C) Silicon due to its large size does not form π-bond with oxygen. The hydrolysis products of $(Me)_2SiCl_2$ are polymeric silicones.

4.(C) pK_a order is
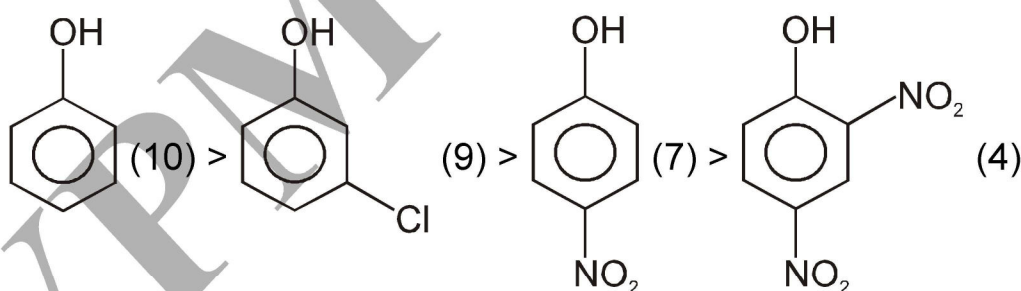
5.(B) D-glucopyranose is cyclic form of glucose. Around C-1 (Newly formed chiral centre, due to cycle formation) two isomers are observed. They are called as α and β-Anomers.

6.(C) Due to ortho effect o-hydroxybenzoic acid is the strongest acid and correct order of decreasing K_a is.

7.(A) For fcc $\rightarrow$ $\sqrt{2}a = 4r = 2d$

so d = $\dfrac{\sqrt{2}a}{2}$

8.(A) $V_m = \dfrac{V}{n}$ & $Z = \dfrac{PV_m}{RT}$ & $V_m = 11b$

$Z = 1 + \dfrac{Pb}{RT} = 1 + \dfrac{RT}{10b} \cdot \dfrac{b}{RT} = \dfrac{11}{10} = 1.1$

9.(B) $\Delta H = nC_p\Delta T = 3 \times 75 \times (75 - 15) = 3 \times 75 \times 60 = 13.5$ kJ

10.(D) Adding reactant will drive the reaction in forward direction in order to restore equilibrium. Therefore, addition of CO(g) will increase the equilibrium amount of CO_2.

11.(D) Absorbance, $A = \log\dfrac{I_0}{I} = \log\dfrac{100}{19.2} = 0.717$

$\varepsilon = \dfrac{A}{lc} = \dfrac{0.717}{(1\,cm)(5 \times 10^{-4}\,mol/L)} = 1.43 \times 10^3$ L mol^{-1} cm^{-1}

12.(B) There are two tetrahedral in a cube so

$\Delta_{cubic} = 2\Delta_t$ $\boxed{\Delta_t = \dfrac{4}{9}\Delta_0}$

$\Delta_{cubic} = 2 \times \dfrac{4}{9}\Delta_0$ $\boxed{\Delta_{square\ planar} = 1.3\Delta_0}$

$\Delta_{cubic} = \dfrac{8}{9}\Delta_0$

13.(D) For ^{3}D spin multiplicity is 3

$(2S + 1) = 3$ $\qquad L \Rightarrow$ $0 = S$

$1 = P$

$2 = D$

$3 = F$

then $2S = 4$

$\boxed{S = 2}$

For D total angular momentum

quantum number L = 2

$J_{possible} \Rightarrow$ $(L + S)$ --------- $(L - S)$

$(2 + 2)$ $(2 - 2)$

4 3 2 1 0

$J_{valid} \Rightarrow$ $(2S + 1) \Rightarrow 5$ All J are valid

J_{useful} can be 4 ($^3D_4$) and 0 ($^3D_0$).

4 not present in option so Ans. is $^3D_0$.

14.(B) $[TeF_5]^- = AB_4LF^-$

Steric No. = $\dfrac{6+5+1}{2}$ = 6

Geometry = sp^3d^2

Shape = Square Pyramidal

15.(A) P_4S_3 =
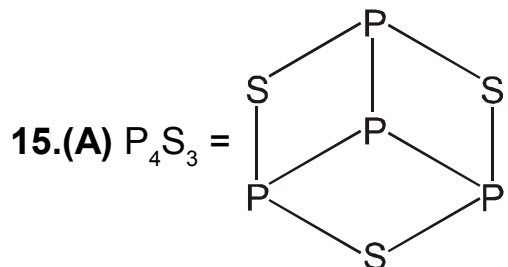
No. of P-S bonds = 6

No. of P-P bonds = 3.

16.(C) The following electronic configurations show orbital contribution to the magnetic moment in high spin octahedral complexes —

d^1, d^2, d^6, d^7

$[Cu(H_2O)_6]^{2+} \rightarrow$ C.M.I. $\rightarrow d^9$, H.S.

$[Ni(H_2O)_6]^{2+} \rightarrow$ C.M.I. $\rightarrow d^8$, H.S.

$[Co(H_2O)_6]^{2+} \rightarrow$ C.M.I. $\rightarrow d^7$, H.S. $\rightarrow$ show orbital contribution.

$[Cr(H_2O)_6]^{2+} \rightarrow$ C.M.I. $\rightarrow d^4$, H.S.

17.(A)

18.(A)

$$\xrightarrow[\text{THF,0 °C}]{\text{LiAlH}_4 \text{ (1 equiv.) (Axial Side attack)}}$$
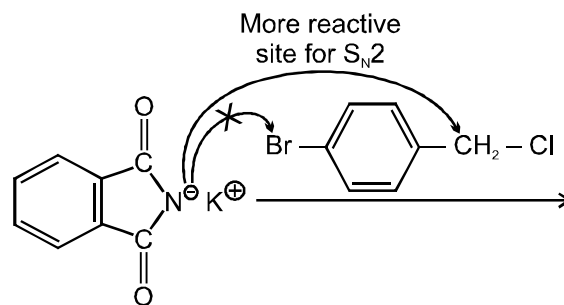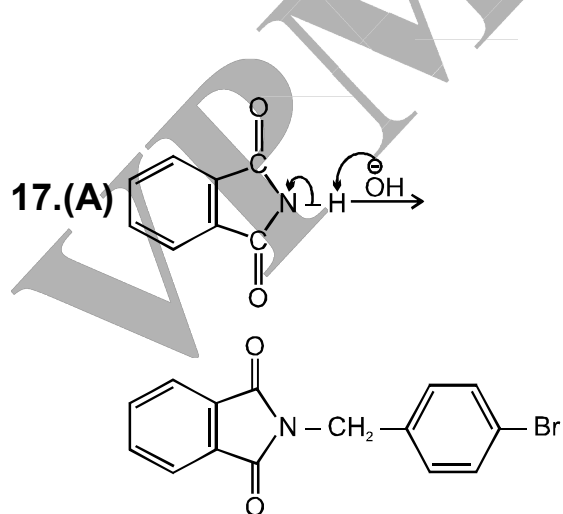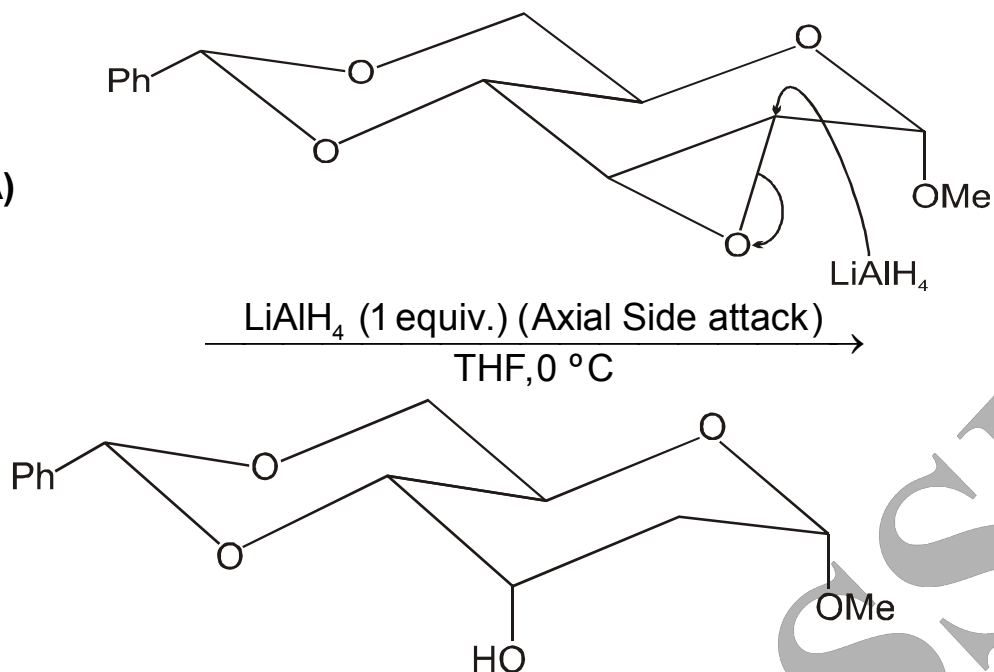
In this reaction, the reagent LiAlH₄ attacks from axial side to give the major product in which in the OH group lies in axial side & is stabilized by H-Bonding.

19.(B)

$$\xrightarrow[\substack{\text{intramolecular}\\ \text{Cannizaro reaction}}]{\text{OH}^-/100}$$

$$\xrightarrow{\text{H}^+/\text{H}_2\text{O}}$$

20.(A)

(At lower pH Dication) $\xrightarrow[\text{at pH}-10]{-3\text{H}^+}$

(At higher pH Monoanion)

At pH-10 all H⁺ of tryptophan are lost and the monoanion exists.

21.(C)

22.(A) In C = C – C = O system as solvent polarity increases, the resonating structure II is more favoured, so the n-π* transitions undergo hypsochromic shift, while the π-π* transitions undergo bathochromic shift.

 (I) ↔ **(II)** more stable in polar solvent.

23.(D) $AgNO_3 + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

Initially there is aq. KCl solution now as solution of $AgNO_3$ is added, AgCl(s) is formed. Hence conductivity of solution is almost compensated (or slightly increase) by the formation of KNO_3. After end point conductivity increases more rapidly because of the addition of excess $AgNO_3$ solution.

24.(D) At initial stage

Clay	Silica	Water
100 – (45% + 12%)	45%	12%
= 43%		

At final stage :

Let   silica = x%

water = 8% (given)

clay = (92 − x)%

Ratio of silica & clay will remain same

before & after drying

$$\Rightarrow \frac{45}{43} = \frac{x}{(92 - x)} \Rightarrow x = 47\%$$

25.(B)

$$\varepsilon_V = \left(V + \frac{1}{2}\right)\omega_e - \left(V + \frac{1}{2}\right)^2 \omega_e Xe$$

For V = 0

$$\varepsilon_{V = 0} = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e Xe = \frac{1}{2} \times 2330 \text{ cm}^{-1} - \frac{1}{4} \times 56 \text{ cm}^{-1} = 1165 \text{ cm}^{-1} - 14 \text{ cm}^{-1}$$

$$\boxed{\varepsilon_{V=0} = 1151 \text{ cm}^{-1}}$$

For IInd level V = 1

$$\varepsilon_{V = 1} = \left(1 + \frac{1}{2}\right)\omega_e - \left(1 + \frac{1}{2}\right)^2 \omega_e Xe = \frac{3}{2}\omega_e - \frac{5}{4}\omega_e Xe$$

$$= \frac{3}{2} \times 2330 \text{ cm}^{-1} - \frac{5}{4} \times 56 \text{ cm}^{-1} = 3495 \text{ cm}^{-1} - 70 \text{ cm}^{-1}$$

$$\boxed{\varepsilon_{V=1} = 3425 \text{ cm}^{-1}}$$

Spacing = $\varepsilon_{V = 1} - \varepsilon_{V = 0}$ = 3425 cm^{-1} − 1151 cm^{-1} = 2274 cm^{-1}.

26.(A) The rate of reaction is —

$$R = \frac{d[HCl]}{dt} = K_2[Cl^\bullet][CH_4] \qquad ...(i)$$

Cl$^\bullet$ is intermediate so on applying steady-state approximation —

$$\frac{d[Cl^\bullet]}{dt} = 2K_1[Cl_2] - K_2[Cl^\bullet][CH_4] + K_3[CH_3^\bullet][Cl_2] - 2K_4[Cl^\bullet]^2 = 0 \qquad ...(ii)$$

$$\frac{d[CH_3^\bullet]}{dt} = K_2[Cl^\bullet][CH_4] - K_3[CH_3^\bullet][Cl_2] = 0$$

$[CH_3{}^\bullet] = \dfrac{K_2[Cl^\bullet][CH_4]}{K_3[Cl_2]}$ ...(iii)

Substituting the value of eq.(iii) into eq.(ii) —

$0 = 2K_1[Cl] - K_2[Cl^\bullet][CH_4] + K_3\left(\dfrac{K_2[Cl^\bullet][CH_4]}{K_3[Cl_2]}\right)[Cl_2] - 2K_4[Cl^\bullet]^2$

$0 = 2K_1[Cl_2] - 2K_4[Cl^\bullet]^2$

$[Cl\cdot] = \dfrac{K_1}{K_2}[Cl_2]^{\frac{1}{2}}$ ...(iv)

From eq. (iv) & (i) —

$$\boxed{R = K_2\left(\dfrac{K_1}{K_4}\right)^{\frac{1}{2}}[CH_4][Cl_2]^{\frac{1}{2}}}$$

27.(C) $K_h = \dfrac{K_w}{K_a \times K_b}$

$K_h' = \dfrac{h^2}{(1-h)^2}$

$\dfrac{h}{1-h} = \sqrt{\dfrac{K_w}{K_a.K_b}} = \sqrt{\dfrac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.38 \times 10^{-10}}} = 1.219$

h = 0.5495

% hydrolysis = 54.95%.

28.(A) Energy of Ground state = E_0 = 1

Energy of first excited state = E_1 = 1×10^{-20} J

Energy of second excited state = E_2 = 3×10^{-20} J

T = 298 K

Population between two states —

$\dfrac{N_j}{N_o} = \exp\left(-\dfrac{\Delta E}{K_B T}\right)$

Population ratio between ground and Ist excited state

$\dfrac{N_1}{N_0} = \exp\left(-\dfrac{1 \times 10^{-20}}{1.38 \times 10^{-23} \times 298}\right)$ = exp(–2.4317) = 0.0879

$N_0 : N_1$ = 1 : 0.0879

Population ratio between Ist and IInd excited states —

$\dfrac{N_2}{N_1} = \exp\left(-\dfrac{2 \times 10^{-20}}{1.38 \times 10^{-23} \times 298}\right)$ = exp(–4.8633) = 0.0077

$N_1 : N_2 = 1 : 0.0077$

So, $N_0 : N_1 : N_2 = 1 : 0.0879 : (0.0077 \times 0.0879)$

$N_0 : N_1 : N_2 = 1 : 0.0879 : 0.000679$

On dividing by 1.088

$N_0 : N_1 : N_2 = 0.919 : 0.081 : 0.0006$

$\boxed{N_0 : N_1 : N_2 = 0.919 : 0.081 : 0.001}$

29.(A) The pH point from where the ionisation of the acid starts is approximately equal to its pk_a, so in this case $pH_1 = pKa$.

30.(C) The differential rate expansions of this reactions are –

$$\frac{d[A]}{dt} = -K_A[A] \; ; \; \frac{d[I]}{dt} = -K_A[A] - K_I[I],$$

$$\frac{d[p]}{dt} = K_I[I]$$

Applyine stead state approximation to differential rate expression for I.

$$\frac{d[I]}{dt} = -\;0 \;\; K_A[A] - K_J[I]$$

$$= \;\; \frac{K_A}{K_I} = \frac{[I]}{[A]}$$

$$= \;\; \frac{K_A}{K_I} = [A] \;\; = \;\; \frac{K_A}{K_I}[A] \circ e^{-kAt} \; [I]$$

Rate of reaction

$$\frac{d[p]}{dt} = K_I[I] \;\; = \frac{K_A}{K_I}(K_I[A] \circ e^{-kAt})$$

$$\int_0^{[p]} d[p] = K_A[A] \circ \int_0^t e^{-kAt}$$

$$[p] = K_A[A] \circ \left[\frac{1}{K_A}(1 - e^{-kAt}) \right]$$

$$[p] = [A] \circ (1 - e^{-kAt})$$

31.(A.D) (X)

NaNH$_2$(Base)

(–H$^+$)

(Resonance Stabilized Anion)

(Y)

NaNH$_2$(Base)

(–H$^+$)

(Antiaromatic Anion)
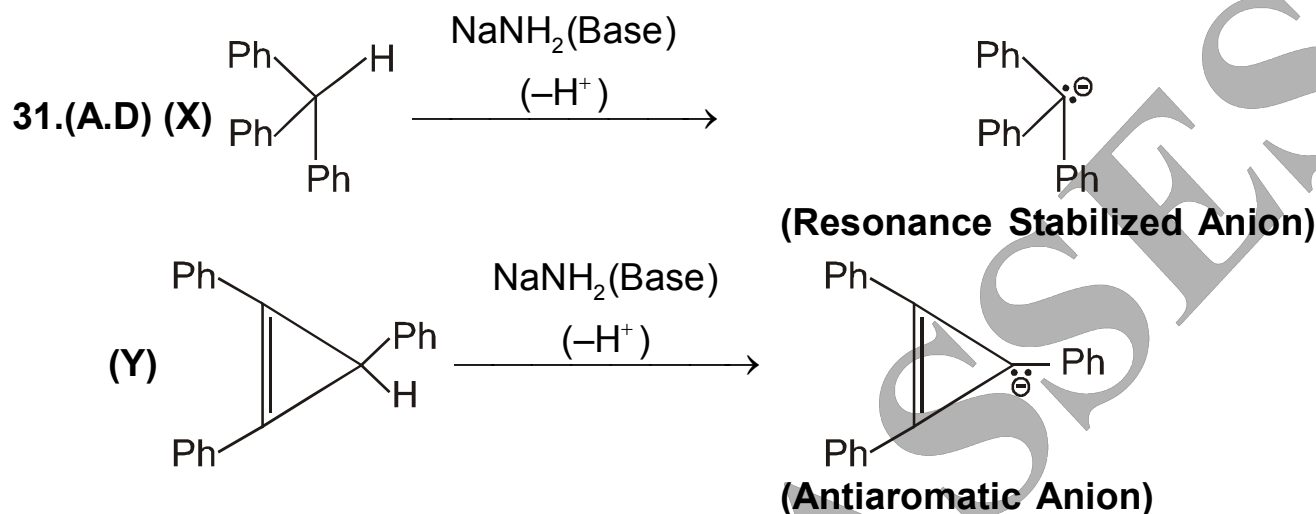
So (X) is a stronger bronsted acid (H$^+$ donor) than (Y) and reacts faster than (Y) with a base.

32.(D) (X) $\equiv$

(Y) $\equiv$
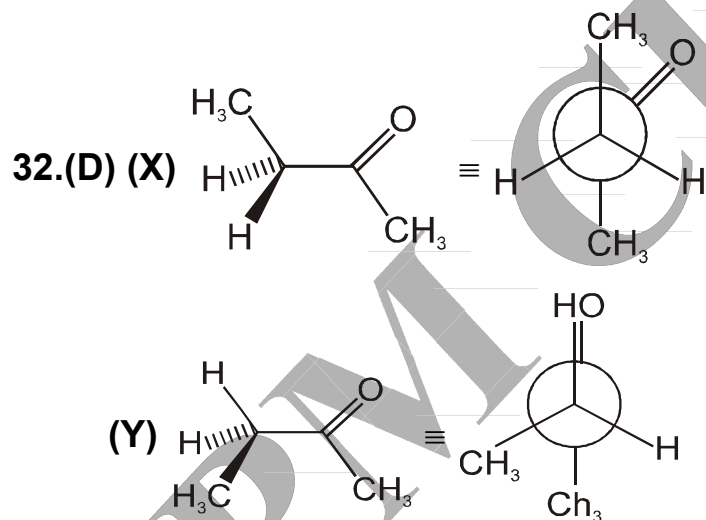
In conformation (X), the methyl groups are anti so it is more stable conformation than (Y), where these two groups have gauche conformation.

33.(A,B,C,D)

(I) 1736 > (II) 1718 (Keto-enol form)

(I) 1738 (H-b) < (II) 1760

(I) 1686 (Steric Crowding) < (II) 1693

(I) –I effect of F groups > (II) +I effect of CH$_3$ group.

34.(A,B,D) (A) 1st compound has zero dipole moment.

(B) EWG (O, Cl) are in the same direction.

(D) –COOH group with draws more –ve charge. So charge separation will increase.

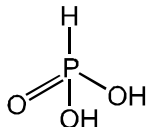**35.(B,C,D)** The structure of H_3PO_3 is as follows : There are only two –OH groups and hence dibasic. The oxidation number of P in this acid is +3. Whereas P may have +5 oxidation state also. Therefore, H_3PO_3 can be oxidized which means H_3PO_3 is a reducing agent.

36.(C,D) In Cis - $[Co(NH_3)_4 cl_2]$ and trans - $[Co(en)_2 cl_2]$ place of symmetry is present so optically inactive.

In Cis-$[Co(en)_2cl_2]$ and $[Co(en)_3]^{3+}$ plane of symmetry and centre of symmetry are absent so they are optically active.

37.(A,B) Boron Nitride and Graphite have staked layer structures.

38.(A,B,C) 75 mL $\frac{M}{5}$ HCl = 15 mmol HCl

25 mL $\frac{M}{5}$ NaOH = 5 mm NaOH

After neutralization, 10 mmol HCl will be remaining in 100 mL of solution.

$\Rightarrow$ Molarity of HCl in the final solution = $\frac{10}{100}$ = 0.10

pH = –log[H⁺] = –log (0.10) = 1

39.(A,D) For the given cell, we have

Electrode	Reaction	Potential
Right (1 M calomel)		$E_{calomel} = E^o_{calomel}$
Left (quinhydrone)	$\frac{1}{2}Q + H^+ + e^- = \frac{1}{2}QH_2$	$E_{Q,QH_2,H^+|Pt} = E^o_{Q,QH_2,H^+|Pt}$
		$-\frac{RT}{F}\ln\frac{1}{a_{H^+}}$

The emf of the cell is

$$E_{cell} = E^o_{calomel} - E_{Q,QH_2,H^+|Pt} = (E^o_{calomel} - E^o_{Q,QH_2,H^+|Pt}) + \frac{RT}{F}\ln\frac{1}{a_{H^+}}$$

At 298 K, we have

$$E_{cell} = (E^o_{calomel} - E^o_{Q,QH_2,H^+|Pt}) + (0.05913 \text{ V})pH$$

= (0.280 V – 0.6996 V) + (0.05913 V) pH = –0.4196 V + (0.05913 V) pH

Thus, we have

E_{cell} = –0.4196 V + (0.05913 V) × 5 = –0.1239 V

pH = $\dfrac{1}{(0.05913 \text{ V})}(E_{cell} + 0.4196 \text{ V}) = \dfrac{0.4196 \text{ V}}{0.05913 \text{ V}}$ = 7.1

40.(A,C)

Calculating $\sin^2 \theta$, we have

Angle	$\sin \theta$	$\sin^2 \theta$
21.65°	0.368 9	0.136 1
25.21°	0.425 8	0.181 3
37.06°	0.602 4	0.362 9
44.96°	0.706 5	0.499 1
47.58°	0.738 1	0.544 8

Taking the ratios of $\sin^2 \theta$, we get

0.1361 : 0.1813 : 0.3629 : 0.4991 : 0.5448

or $\quad$ 3 ×0.045 : 4 ×0.045 : 8 × 0.045 : 11× 0.045 : 12 × 0.045

that is $\quad$ 3K : 4K : 8K : 11K : 12K, where K = 0.045

From these ratios, it is obvious that copper has face-centred cubic crystal.

Since $\quad K = \dfrac{\lambda^2}{4a^2}$

therefore,

$a = \left(\dfrac{\lambda^2}{4K} \right)^{1/2} = \dfrac{\lambda}{2} \cdot \dfrac{1}{\sqrt{K}} = \dfrac{154.05 \text{ pm}}{2 \times \sqrt{0.045}} = \dfrac{154.05 \text{ pm}}{2 \times 0.2121} = 363.2 \text{ pm}$

In a face-centred cubic lattice, atoms touch one another along face-diagonal.

Therefore, $\quad 4r = \sqrt{2}\,a \quad$ or $\quad\quad\quad r = \dfrac{\sqrt{2}\,a}{4}$

substituting the values, we have

$$r = \frac{(1.414)(363.2\,\text{pm})}{4} = 128.3\,\text{pm}$$

41.   53

$$\ln\frac{K'}{K} = \frac{\Delta H_r^o}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

$$\Delta H_r^o = \frac{R\ln\left(\dfrac{K'}{K}\right)K}{\left(\dfrac{1}{T} - \dfrac{1}{T'}\right)}$$

$$\Delta H_r^o = \frac{8.314 \times \ln(2)}{\left(\dfrac{1}{298} - \dfrac{1}{308}\right)} = 53\ \text{kJ mol}^{-1}$$

42.   −0.79

Concentration of zinc sulphate solution = 0.1 M; Percentage dissociation = 95

$\therefore$ $[Zn^{2+}]$ = 0.1 × $\dfrac{95}{100}$ = 0.095 M

The electrode reaction in this case is

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad \text{(i.e., n = 2)}$$

According to the Nernst equation, the potential of the electrode is given by

$$E_{el} = E_{el}^o - \frac{RT}{nF}\ln\frac{1}{[Zn^{2+}]} = E_{el}^o + \frac{RT}{nF}\ln[Zn^{2+}] = E_{el}^o + \frac{0.0591}{n}\log[Zn^{2+}]\ \text{at 25°C}$$

Substituting the various values in the above equation,

$$E_{el} = -0.76 + \frac{0.0591}{2}\log 0.095 = \textbf{−0.79 volt.}$$

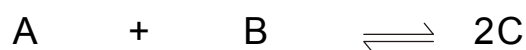**43.   0.3333**

Use $\left(\dfrac{\partial P}{\partial V_m}\right) = 0$ & $\left(\dfrac{\partial^2 P}{\partial V_m^2}\right) = 0$ to get

$$P_c = \frac{B^3}{27C^2};\ V_c = \frac{3C}{B}\ \text{and}\ T_c = \frac{B^2}{3RC}$$

Now, $P_c V_c = Z_c R T_c$ $Z_c = \dfrac{P_c V_c}{RT_c} = \dfrac{1}{3}$ or 0.3333

44.   2.4

$$A \quad + \quad B \quad \rightleftharpoons \quad 2C$$

| Initial mole | 2 | 3 | 0 |
| Mole at equilibrium | $(2 - x)$ | $(3 - x)$ | $2x$ |

$$\therefore \quad K_C = \frac{[C]^2}{[A][B]} = \frac{4x^2 \cdot V \cdot V}{V^2(2-x)(3-x)} \qquad [C] = \frac{2x}{V}$$

$$4 = \frac{4x^2}{(2-x)(3-x)} \qquad\qquad [A] = \frac{2-x}{V}$$

$$\therefore \quad x^2 = 6 - 5x + x^2 \qquad\qquad [B] = \frac{3-x}{V}$$

$$\therefore \quad x = 1\cdot2$$
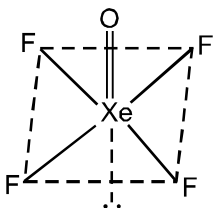
Mole of C at equilibrium = $2x = 2 \times 1.2 = 2.4$

45.   1

$XeOF_4$ has 1 lone pair

$XeOF_4$ — sp^3d^2 Hybridisation [bp= 5 ; lp=1]

Shape - Square pyramidal

Square pyramidal

46.   30

The fundamental bands for nonlinear molecule is : $(3n - 6)$

Number of atoms (n) = 12

Total degrees of freedom = $3n = 3 \times 12 = 36$
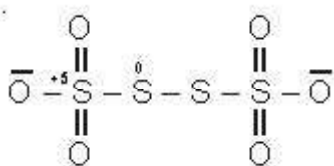
Translational degrees of freedom = 3

Rotational degrees of freedom = 3 (non-linear)

Vibrational degrees of freedom = $36 - 3 - 3 =$ **30**

So there should be 30 fundamental bands in the IR spectrum of benzene.

47.   5

Hints : Structure of $S_4O_6^{2-}$ is

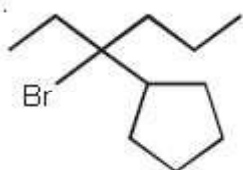$\therefore$ Difference in oxidation state is $+5 - 0 = +5$.

48. **6**

Hints : A decapeptide will have (9) peptide linkage

Mass of hydrolyzed product is (796 + 162) gm/mole

(9 H_2O Molecules used, so 18X 9= 162 added)

Number of glycine molecule = $\frac{0.47 \times 958}{75} = 6$
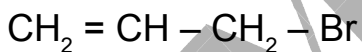
49. **5**

Hints :

3-bromo-3-cyclopentylhexane
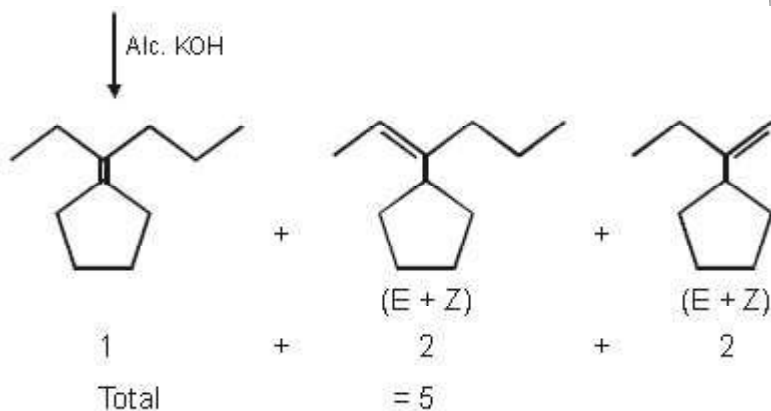
Dehydrobromination of alkyl bromides in the presence of alc. KOH follows E2 mechanism. Hence no rearrangement in alkyl chain is possible.
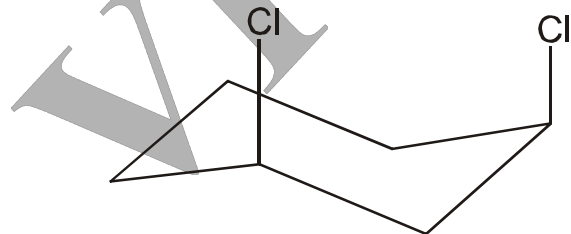
50. **21**

$CH_2 = CH - CH_2 - Br$

Vibration modes = 3N – 6   (N = 9)

= 27 – 6 = **21 Ans.**

51. **3**

[cis-1,3-Dichlorocyclohexane(a,a)meso]

— trans-1,3-Dichlorocyclohexane (a, e)
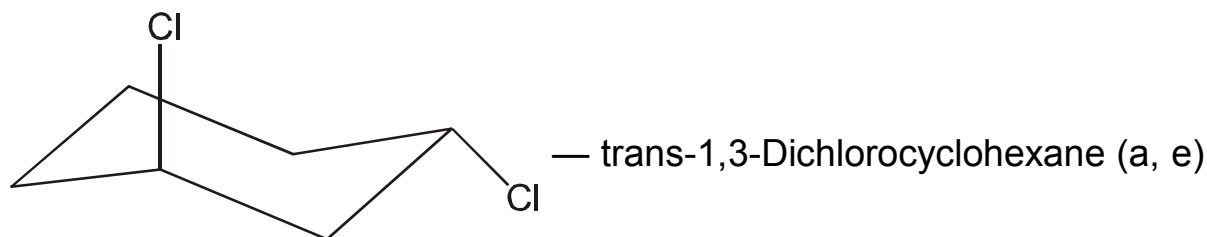
(d) + ($\boldsymbol{l}$) (enantiomers)

Total number of stereoisomers :   cis-isomer (only 1 meso)

trans-isomer (d + $\boldsymbol{l}$ = 2)

= 1 + 2 = 3

52.   3.495

Absorbance A = $\varepsilon C \boldsymbol{l}$

$$A = \log \frac{I_o}{I_t} \quad \begin{bmatrix} I_o = \text{Intensity of initial light} \\ I_t = \text{Intensity of transmitted light} \end{bmatrix}$$

$$A = \varepsilon C \boldsymbol{l} = \log \frac{I_o}{I_t} = \log \frac{1 \times 100}{I_t / I_o \times 100} = \log \frac{100}{\%T} = \log 100 - \log \%T = 2 - \log \%T$$

1 mm = .1 cm

$$\varepsilon = \frac{2 - \log 20}{.1\,\text{cm} \times 2\,\text{mol ltr}^{-1}} = \frac{2 - 1.3010}{.2} = \frac{.699}{.2} = 3.495 .$$

53.   0.10

Crotonic acid is formed as follows :

$\text{HCl} + \text{NaZ} \longrightarrow \text{NaCl} + \text{HZ}$ **(crotonic acid)**

where Z stands for crotonate ion.

Crotonic acid is a weak organic acid and HCl, NaZ and NaCl are strong electrolytes. Hence, using Kohlraush's law of independent migration of ions,

$\Lambda^{\circ}_{mHZ} = \Lambda^{\circ}_{mHCl} + \Lambda^{\circ}_{mNaZ} - \Lambda^{\circ}_{mNaCl}$ = (425 + 80 – 125) × 10^{-4} S m^2 mol^{-1} = 380 × 10^{-4} S m^2 mol^{-1}

Also, at the given concentration of crotonic acid,

$$\Lambda_m = \frac{\kappa}{c} = \frac{3.8 \times 10^{-3}\,\text{S m}^{-1}}{0.001 \times 10^3\,\text{mol m}^{-3}} = 38.0 \times 10^{-4}\,\text{S m}^2\,\text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{38.0 \times 10^{-4}\,\text{S m}^2\,\text{mol}^{-1}}{380 \times 10^{-4}\,\text{S m}^2\,\text{mol}^{-1}} = \mathbf{0.10}$$

54.   8000

Initial conditions   Final conditions

P_1 = 2 atm $\qquad\qquad\qquad$ P_2 = 0·5 atm

V_1 = 1000 mL $\qquad\qquad$ V_2 = ?

T_1 = – 73°C = (–73 + 273)k $\qquad$ T_2 = 123°C = (123 + 273)

= 200 K $\qquad\qquad\qquad\qquad\qquad$ 400 K

We known that $\qquad \dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

So $\quad \dfrac{2 \times 1000}{200} = \dfrac{0.5 \times V_2}{400}$ $\quad$ or $\quad V_2 \times \dfrac{2 \times 1000 \times 400}{200 \times 0.5}$ = 8000 mL

55. 65.71

Total vapour-pressure of solution :

$P = P^{\circ}_{\epsilon t} X_{\epsilon t} + P^{\circ}_{Mt} X_{Mt}$

$P^{\circ}_{\epsilon t}$ = Vapour pressure of Ethanol = 44.5 mm of Hg

P°_{mt} = Vapour pressure of Methanol = 88.7 mm of Hg

$X_{\epsilon t}$ = Mole fraction of ethanol

X_{mt} = Mole fraction of methanol

$\Rightarrow n_{\epsilon th} = \dfrac{60}{46}$ $\quad$ (M.W. of ethanol = 46)

$\qquad\quad$ = 1.30 mol

$n_{meth} = \dfrac{40}{32}$ $\qquad$ (M.W. of methanol = 32)

$\qquad\quad$ = 1.25 mol

$x_{eth} = \dfrac{1.30}{1.30 + 1.25} = 0.50$

$X_{meth} = \dfrac{1.25}{1.25 + 1.30} = 0.49$

P = 44.5 × 0.50 + 88.7 + 0.49 = 65.71 mm of Hg

56. 2

The general expression for the half-life of a reaction of the type $A \rightarrow P$ is

$t_{\frac{1}{2}} = \dfrac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$ = f(n, k)$[A]_0^{1-n}$

where $f(n, k) \dfrac{2^{n-1} - 1}{(n-1)k}$.

Then $\quad \log t_{\frac{1}{2}}$ = log f + (1 – n)log $p_0[p_0 \times [A]_0]$

Hence, $\log\left(\dfrac{t_{\frac{1}{2}}(p_{0,1})}{t_{\frac{1}{2}}(p_{0,2})}\right)$ = (1 – n)$\log\left(\dfrac{p_{0,1}}{p_{0,2}}\right)$ = (n – 1)$\log\left(\dfrac{p_{0,2}}{p_{0,1}}\right)$ or

$$(n - 1) = \frac{\log\left(\frac{410}{880}\right)}{\log\left(\frac{169}{363}\right)} = 0.999 = 1$$

Therefore, n = 2.

57. **8**

$$J_{max} = \left(\frac{kT}{2hcB}\right)^{1/2} - \frac{1}{2} = \left[\frac{(1.38 \times 10^{-23}\,JK^{-1})(300\,K)}{2(6.626 \times 10^{-34}\,Js)(3 \times 10^{10}\,cms^{-1})(1.566\,cm^{-1})}\right]^{1/2} - \frac{1}{2}$$

$$= 7.56 = 8$$

58. **13**

$$\delta = \frac{\nu_{sample} - \nu_{reference}}{\text{operating frequency}} \times 10^6 \text{ ppm} = \frac{\Delta\nu \times 10^6}{\text{operating frequency}} \text{ppm}$$

$$= \frac{-1200 \times 10^6}{400 \times 10^6} \text{ppm} = -3$$

$\tau + \delta = 10$

$\tau = 10 - \delta = 10 - (-3) = $ **13**

59. **5.2**

$$pI = \frac{pka + pka'}{2}$$

pka = 5.7

pka' = 14 - pkb = 14 - 9.3 = 4.7

$$pH = \frac{5.7 + 4.7}{2} = \frac{10.4}{2} = 5.2$$

60. **1**

$$A = \log\frac{I_0}{I_t} = \varepsilon\ell C$$

$$\log\frac{I_0}{I_0/10} = \varepsilon\ell C \quad I_t = \frac{I_0}{10}$$

$\log 10 = \varepsilon \times 20\,cm \times .05\,mol\,liter$

$$\varepsilon = \frac{\log 10}{20\,cm \times .05\,M} = \frac{1}{20\,cm \times .05\,M} = 1 = 1\,\text{mole liter cm}^{-1}$$