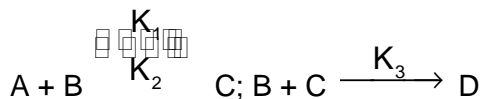


PART-A (1-20)

1. At what temperature root mean square speed of N_2 gas is equal to that of propane gas at S.T.P. conditions ?
 (A) 173.7°C (B) 173.7 K (C) S.T.P. (D) -40°C

2. For the reaction scheme



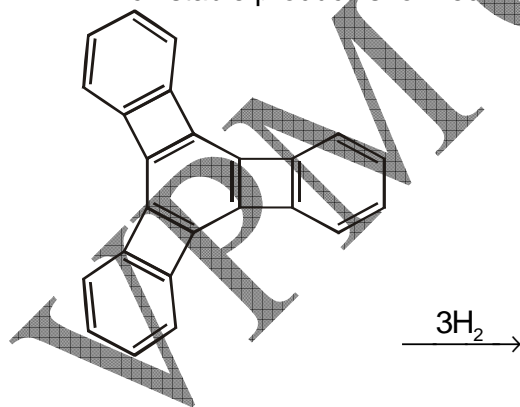
the rate equation for the formation of D is given as —

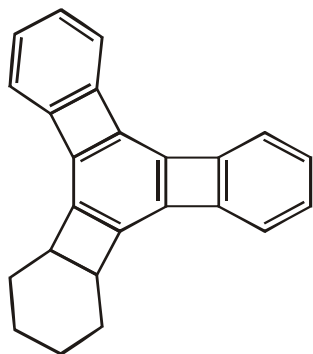
- (A) $\frac{d[D]}{dt} = \frac{K_1 K_3 C_A C_B}{K_2 + K_3 C_B}$ (B) $\frac{d[D]}{dt} = \frac{K_1 K_2 K_3 C_A C_B}{K_2 + K_3 C_B}$
 (C) $\frac{d[D]}{dt} = \frac{K_1 K_3 C_A C_B^2}{K_2 + K_3 C_B}$ (D) $\frac{d[D]}{dt} = \frac{K_1 K_3 C_A C_B}{K_2 K_3 + K_3 C_B}$

3. Bond energy of H – H, F – F and H – F bonds are 104, 38 and 135 kcal mol⁻¹ respectively. The resonance energy in the H – F molecule is:
 (A) $-72.14\text{ kcal mol}^{-1}$ (B) $72.14\text{ kcal mol}^{-1}$
 (C) $207.14\text{ kcal mol}^{-1}$ (D) $-207.14\text{ kcal mol}^{-1}$

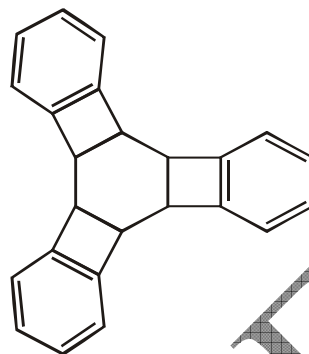
4. Of the following compounds, which will have a zero dipole moment?
 (A) 1, 1-Dichloroethylene (B) *cis*-1, 2-Dichloroethylene
 (C) *trans*-1, 2-Dichloroethylene (D) None of the three.

5. Which stable product is formed in the following reaction ?



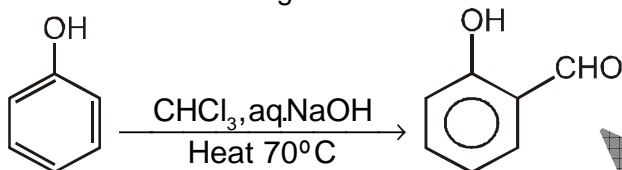


(A)
(C) A & B both



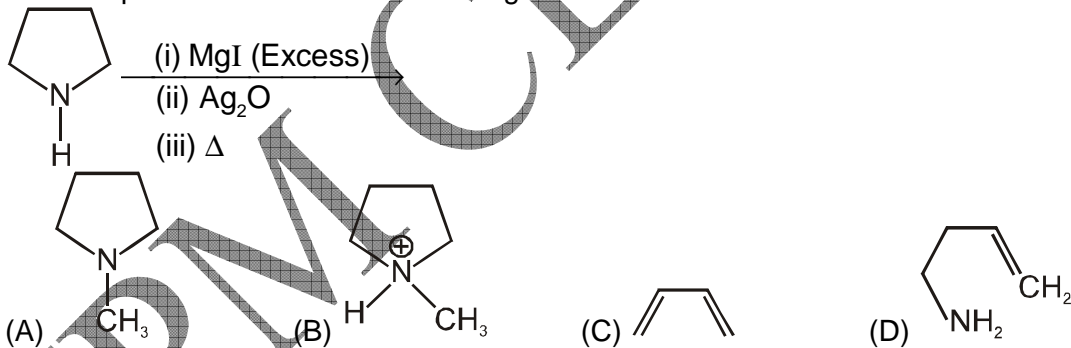
(B)
(D) None of these

6. Consider the following reaction



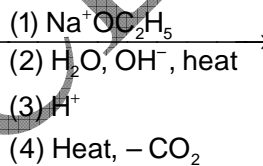
What is the reaction known as and which species does it involve, respectively,
 (A) Sandmeyer, free radical (B) Reimer-Tiemann, carbene
 (C) Hensdiecker, free radical (D) Friedal-Crafts, Carbonium ion

7. The end product formed in the following reaction is :



- (A) B₂ (B) Be₂ (C) Be₂⁺ (D) Li₂

13. The correct order of decreasing second ionisation enthalpy of Ti, V, Cr and Mn is
 (A) V > Mn > Cr > Ti (B) V > Ti > Cr > Mn (C) Cr > Mn > V > Ti (D) Ti > V > Cr > Mn
14. Which of the following complexes exhibits the Highest paramagnetic behaviour?
 (A) [Fe(en)(bpy)(NH₃)₂]²⁺ (B) [V(gly)₂(OH)₂(NH₃)₂]⁺
 (C) [CO(ox)₂(OH₂)]⁻ (D) [Ti(NH₃)₆]³⁺
15. Among the following metal carbonyls, the C – O bond order is lowest in
 (A) [Mn(CO)₆]⁺ (B) [Fe(CO)₅] (C) [Cr(CO)₆] (D) [V(CO)₆]⁻
16. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of
 (A) nitrogen (B) oxygen (C) carbon dioxide (D) argon
17. MgSO₄ on reaction with NH₄OH and Na₂HPO₄ forms a white crystalline precipitate. What is its formula ?
 (A) Mg(NH₄)PO₄ (B) Mg₃(PO₄)₂ (C) MgCl₂.MgSO₄ (D) MgSO₄
18. Which of the following will not react with NaOH to form water ?
 (A) NaH₂PO₃ (B) Na₂HPO₃ (C) Na₂HPO₄ (D) None
19. Identify the compound 'X' in the following reaction :

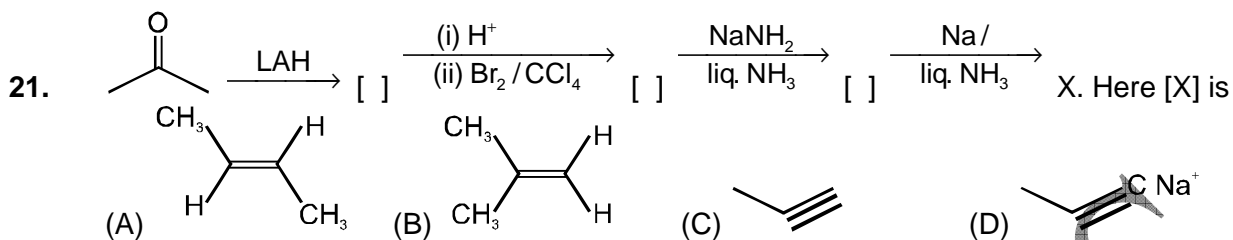


Malonic ester + Isobutyl bromide

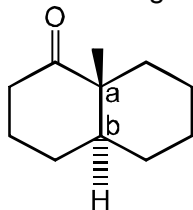
- (A) Isocaproic acid (B) Neocaproic acid (C) Normal caproic acid (D) None of these

20.
$$\begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \end{array} \xrightarrow{\text{bromine water}} \begin{array}{c} \text{COOH} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \end{array} \xrightarrow[\text{(iii) heat}]{\begin{array}{l} \text{(i) lime water} \\ \text{(ii) H}_2\text{O}_2 / \text{Fe}^{3+} \end{array}} \begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_2 \\ | \\ \text{CH}_2\text{OH} \end{array}$$
- [A] [B]. Here [B] is
- (A) $\begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \end{array}$ (B) $\begin{array}{c} \text{COOH} \\ | \\ (\text{CHOH})_3 \\ | \\ \text{CH}_2\text{OH} \end{array}$ (C) $\begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_2 \\ | \\ \text{CH}_2\text{OH} \end{array}$ (D) $\begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{CH}_2\text{OH} \end{array}$

PART-B (21-40)



22. The absolute configurations at the two chiral centers in the following compound



- (A) aR, bS (B) aS, bR (C) aS, bS (D) aR, bR

23. 1 L flask contains nitrogen along with a drop or two of water at 40°C, the total pressure being 760 torr. If all the contents are transferred to another flask of 0.5 L at the same temperature, the pressure set up in the second flask will be (aqueous tension at 40°C = 55 torr)

- (A) 1410 torr (B) 1465 torr (C) 1520 torr (D) none of these

24. If A and B are Hermitian and commute, then the product of AB will be

- (A) 0 (B) 1 (C) Hermitian (D) Anti Hermitian

25. The wave function $\psi_1 = \sqrt{\frac{1}{2\pi}}$ and $\psi_2 = \sqrt{\frac{1}{\pi}} \cos nx$ in the interval 0 to 2π are

- (A) normalized (B) orthogonal (C) cannot be predicted (D) none

26. Consider the cell $\text{Ag} | \text{AgBr}(s) | \text{Br}^- (a = 0.32), \text{Cu}^{2+} (a = 0.42), \text{Cu}^+ (a = 0.36) | \text{Pt}$. The e.m.f. of this cell at 25°C is 0.0565 V. Calculate the standard e.m.f. of the cell.

- (A) -0.031 V (B) 0.031 V (C) -0.818 V (D) 0.818 V

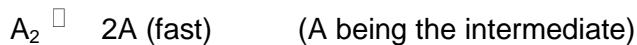
27. Calculate the frequency in wave numbers of the 3rd line in the Pfund series ($n = 5$) in the emission spectrum of atomic hydrogen. ($R = 109677.76 \text{ cm}^{-1}$)

- (A) 2700 cm^{-1} (B) 4400 cm^{-1} (C) 7800 cm^{-1} (D) 12000 cm^{-1}

28. One mole of the ideal gas at 3 atm and 300 K is expanded isothermally to double its initial volume against an external pressure of 1.5 atm. Calculate W.

- (A) 12.3 J (B) 1250 J (C) -12.3 J (D) -1250 J

29. A reaction $A_2 + B \rightarrow \text{Products}$, involves the following mechanism :



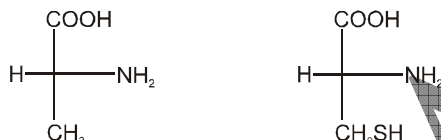
$A + B \xrightarrow{K_2} \text{Products}$ (slow). The rate law consistent to this mechanism is :

- (A) rate = $k[A_2][B]$ (B) rate = $k[A_2]^2[B]$ (C) rate = $k[A_2]^{1/2}[B]$ (D) rate = $k[A_2][B]^2$

30. The vectors $3p\hat{i} + \hat{j} + q\hat{k}$ and $2p\hat{i} + 3\hat{j} + 6q\hat{k}$ are orthogonal, if :
 (A) $p = q$ (B) $p^2 + q^2 = 3$ (C) $p = -q$ (D) Never

31. The relationship between the dissociation energy of N_2 and N_2^+ is
 (A) $N_2 = N_2^+$ (B) Unpredictable (C) $N_2 > N_2^+$ (D) $N_2 < N_2^+$

32. The correct absolute configuration assigned for compound (I) and (II) respectively is –



- (A) R, R (B) R, S (C) S, S (D) S, R

33. The correct order of acidic strength is –

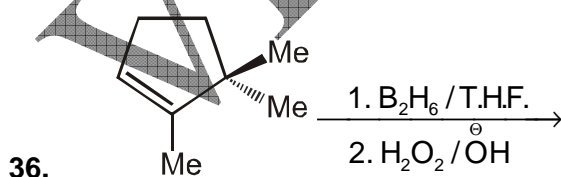
- (A) $\text{SiO}_2 < \text{CO}_2 < \text{N}_2\text{O}_5 < \text{SO}_3$ (B) $\text{SiO}_2 < \text{N}_2\text{O}_5 < \text{CO}_2 < \text{SO}_3$
 (C) $\text{CO}_2 < \text{SiO}_2 < \text{N}_2\text{O}_5 < \text{SO}_3$ (D) $\text{SO}_3 < \text{CO}_2 < \text{N}_2\text{O}_5 < \text{SiO}_2$

34. Which of the following has maximum number of lone pairs on central atom?

- (A) ClO_3^- (B) XeF_4 (C) SF_4 (D) I_3^-

35. Which of the following is an arachno borane –

- (A) $[\text{B}_6\text{H}_6]^{2-}$ (B) $[\text{B}_5\text{H}_9]$ (C) $[\text{B}_2\text{H}_6]$ (D) $[\text{B}_6\text{H}_{12}]$

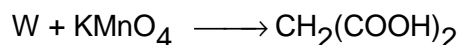
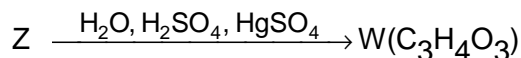
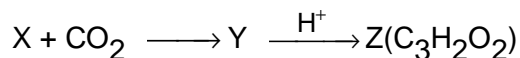


Which of the following is **incorrect** for above reaction:

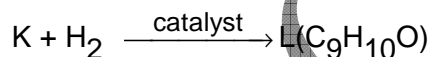
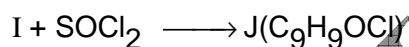
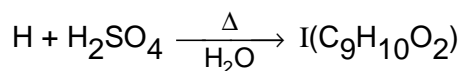
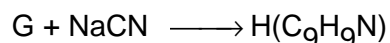
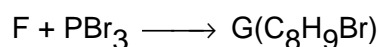
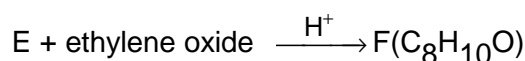
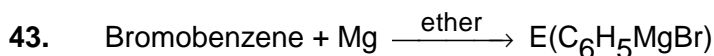
- (A) Product is optically active
 (B) It is an oxidation reaction
 (C) Overall reaction is stereospecific syn addition
 (D) B_2H_6 adds on alkene by forming a cyclic transition state.
37. The Miller indices of crystal plane which cuts through the crystal axis at $2a$, $-3b$, $-3c$ is,
 (A) $2\bar{3}\bar{3}$ (B) $3\ 2\ 6$ (C) $6\ 2\ 3$ (D) $3\ \bar{2}\ \bar{2}$
38. IR spectra of benzaldehyde and acetophenone will show distinguishing peaks in the region
 (A) $3000 - 3600\text{ cm}^{-1}$ (B) $1200 - 1300\text{ cm}^{-1}$
 (C) $2700 - 2800$ and $2860 - 2975\text{ cm}^{-1}$ (D) 1600 and 1740 cm^{-1}
39. Which is **not** correctly matched?
 (A) XeO_3 : trigonal bipyramidal (B) ClF_3 : T shaped
 (C) $XeOF_4$: square pyramidal (D) XeF_2 : linear shape
40. If standard reduction potentials of Ni^{2+}/Ni and Au^{3+}/Au couples are -0.25 V and 1.50 V respectively, then the EMF of the cell
 $Ni/Ni^{2+} (0.01\text{ M}) || Au^{3+} (0.1\text{ M})/Au$ will be
 (A) unpredictable (B) $= EMF^0$ (C) $< EMF^0$ (D) $> EMF^0$

PART-C (41-50)

41. When 16.8 g of white solid, X were heated, 4.4 g of acid gas A, that turned lime-water milky was driven off together with 1.8 g of a gas B which condensed to a colourless liquid. The solid that remained, Y, dissolved in water to give an alkaline solution, which with excess of barium chloride solution gave a white precipitate Z. The precipitate effervesced with acid giving of carbon dioxide. Identify A, B and Y and write down the equation for the thermal decomposition of X.
42. $\text{Acetylene} + CH_3MgBr \longrightarrow X + CH_4$



Identify X, Y, Z, W and write complete reaction equation.

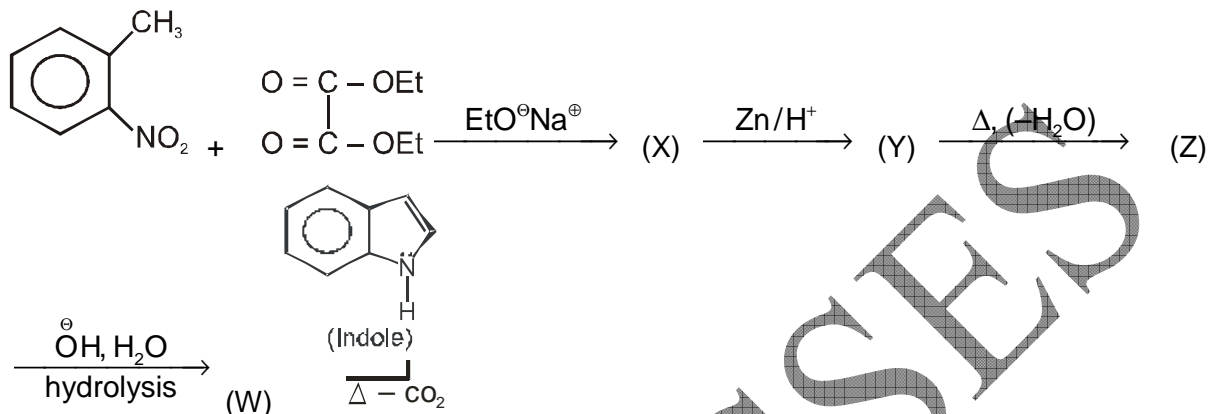


Identify E, F, G, H, I, J, K, L, M and write complete reaction equation.

44. The degree of dissociation of Ca(NO₃)₂ in a dilute aqueous solution, containing 7.0 g of the salt per 100 g of water at 100°C is 70%. If the vapour-pressure of water at 100°C is 760 mm, calculate the vapour-pressure of the solution.

45. Heat of combustion of ethylene (C₂H₄) is – 337 kcal mol⁻¹ under standard state at 298 K. Assuming 70.0% efficiency, how many kg of water at 20°C can be converted into steam at 100°C burning 1.00 m³ of C₂H₄ gas measured at STP? Specific heat of water is 1 kcal kg⁻¹ K⁻¹ and its latent heat of vaporization is 540 kcal kg⁻¹.

46. Identify the intermediate products X, Y, Z and W in the following sequence of reactions.



47. 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 the mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour-pressure of the solution and the mole-fraction of methanol in the vapour.

48. The rate law for the reaction $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ is

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = k[\text{NO}]^2[\text{O}_2]$$

The proposed mechanism is



(a) The reaction mechanism does not include a collision among three molecules. Since the reaction order is three, shouldn't the mechanism include such a collision ?

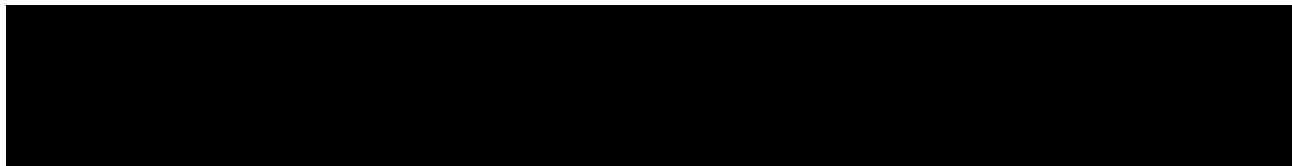
(b) Which step in the proposed mechanism is the slowest step ?

(c) What is the molecularity of each step ?

49. (a) C_v for uranium metal is $3.04 \text{ JK}^{-1} \text{ mol}^{-1}$ at 20K. Calculate the absolute entropy of the metal in $\text{JK}^{-1} \text{ mol}^{-1}$ at 20K.
(b) Calculate the uncertainty in the velocity of an electron if uncertainty in its position is 1 \AA .
50. 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. What will be the slope of this line?

VPM CLASSES

ANSWER KEY



HINTS & SOLUTIONS

- 1.(B) This question is based on the formulae of r.m.s. speed, i.e. $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$

$$u_{\text{rms}}(\text{N}_2) = u_{\text{rms}}(\text{He})$$

$$\sqrt{\frac{3RT}{28}} = \sqrt{\frac{3R \times 273}{44}}$$

$$\frac{273 \times 28}{44} = T$$

or $T = 173.7 \text{ K}$

- 2.(C) $A + B \xrightleftharpoons{K_2} C; B + C \xrightleftharpoons{K_3} D$
Applying the steady state approximation to C,
 $K_1 C_A C_B = K_2 C_C + K_3 C_B C_C$;

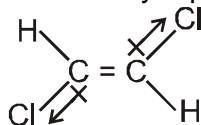
$$\therefore C_C = \frac{K_1 C_A C_B}{K_2 + K_3 C_B}$$

$$\therefore \frac{dC_D}{dt} = K_3 C_B C_C = \frac{K_3 K_1 C_A C_B^2}{K_2 + K_3 C_B}$$

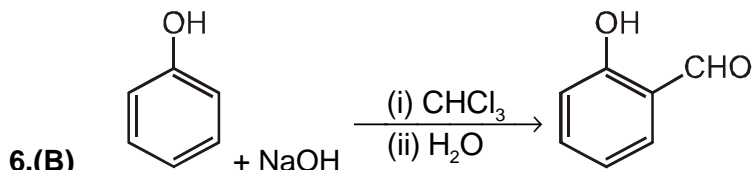
- 3.(B) Resonance energy

$$\Delta H - F = (BE)_{\text{H-F}} - \sqrt{(BE)_{\text{H}_2} (BE)_{\text{F}_2}} = 135 - \sqrt{104 \times 38} = 135 - 62.86 = 72.14 \text{ kcal mol}^{-1}$$

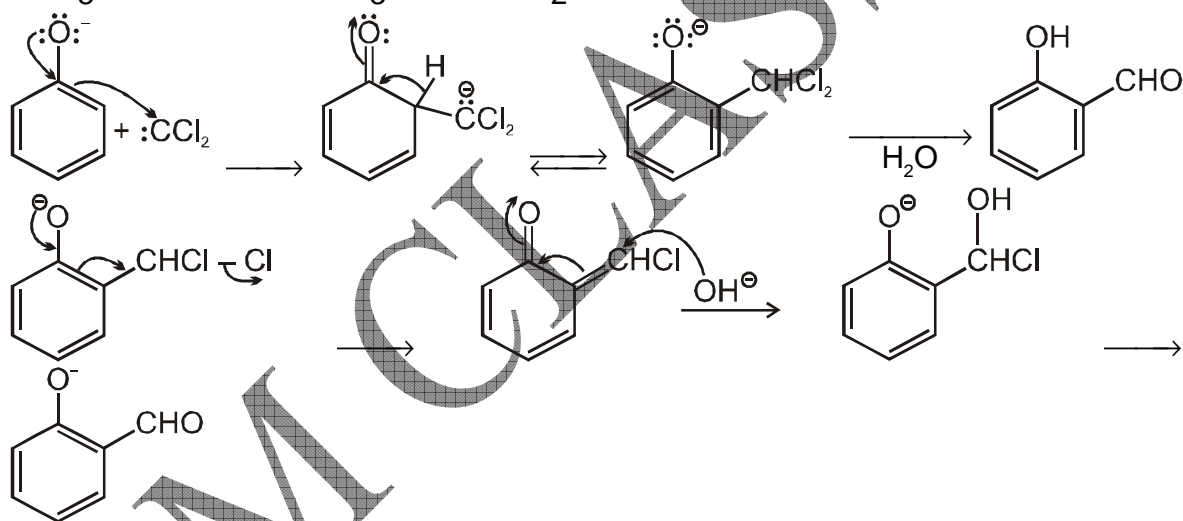
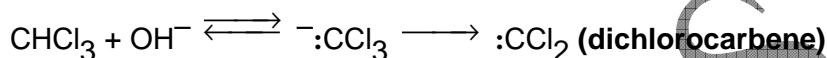
- 4.(C) *trans*-1, 2-Dichloroethylene is symmetrically substituted, dipole moment due to one C – Cl bond is cancelled by equal but opposite dipole moment due to other C – Cl bond.

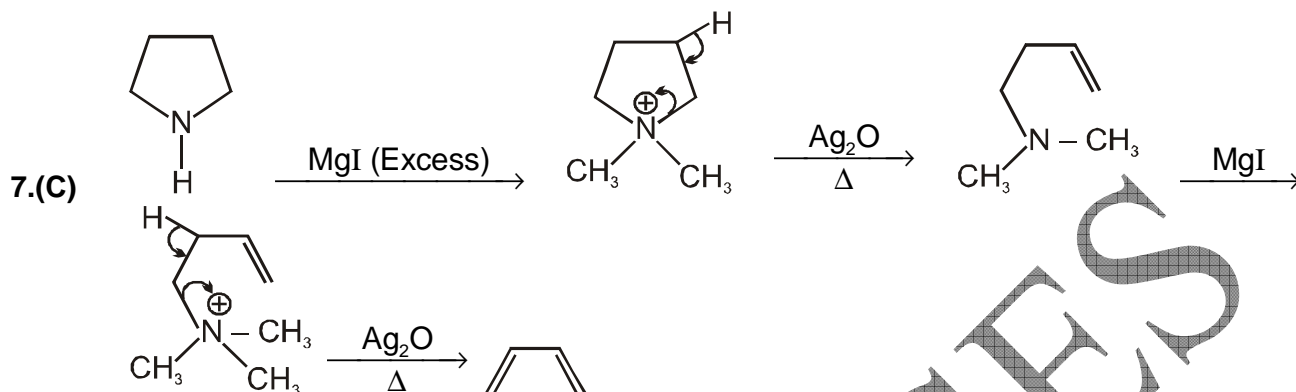


- 5.(B) In product (A), Aromating ring = 3
 Anti Aromatic ring = 2
less stable
- In product (B) has Aromatic ring = 3
 Anti Aromatic ring = 0
Stable

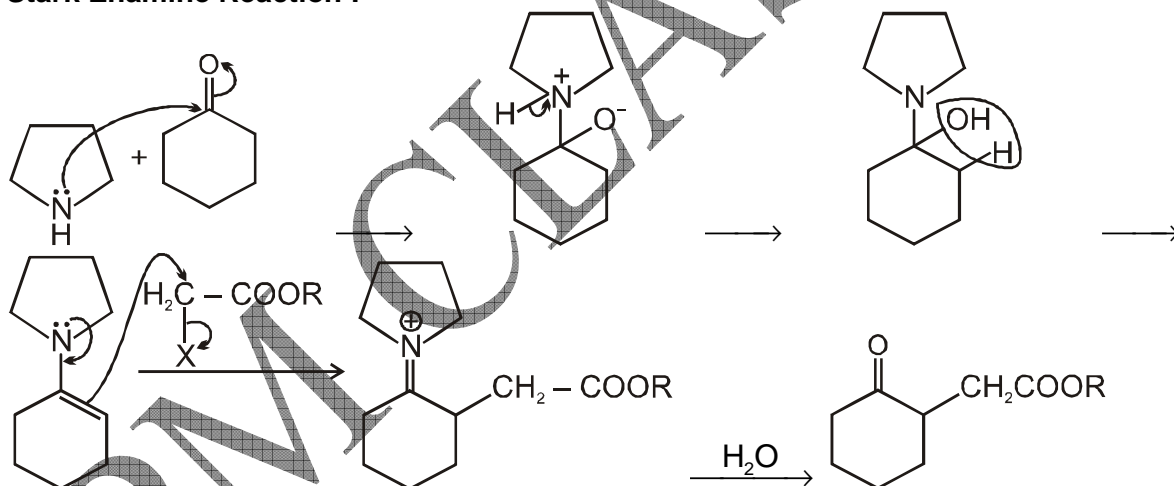


Reimer-Tiemann Reaction

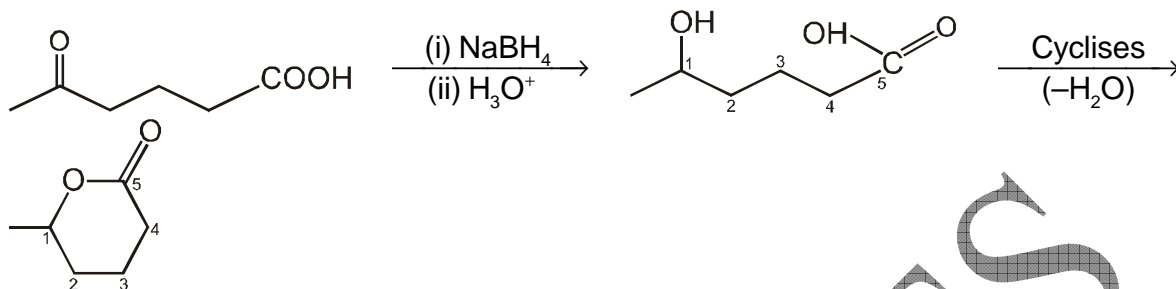




8.(D) Stark Enamine Reaction :



9.(C) NaBH_4 reduces only C = O group and not -COOH group. The product formed undergoes cyclization to form γ -lactone (six-membered rings are formed easily).



10.(C) All salts of alkali metals are highly soluble; solubility of sulphates of alkaline earth decreases down the group.

11.(A) CsCl has body centered cubic structure. A cube has six faces and each cube will have one Cs^+ ion. So, the answer is (A).

12.(B) $\text{Be}_2 = \text{E.C.} - \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$

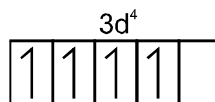
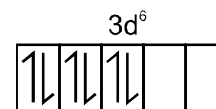
$$\text{B.O.} = \frac{4 - 4}{2} = 0$$
 Be_2 does not exist under normal conditions.

Cr	Mn	V	Ti	
$3d^5 4s^1$	$3d^5 4s^2$	$3d^3 4s^2$	$3d^2 4s^2$	I st I.E.
(Half filled)	$3d^5 > 3d^5 4s^1 > 3d^3 4s^1$	$> 3d^2 4s^1$		II nd I.E.

The second ionisation enthalpy of the first transition series increase almost regularly with increase in atomic number.

14.(C) $[\text{V}(\text{gly})_2(\text{OH})_2(\text{NH}_3)_2]^{3+} = \text{V}^{+5} = 3d^0$ (no unpaired e^-)

$[\text{Fe}(\text{en})(\text{bpy})(\text{NH}_3)_2]^{2+} = \text{Fe}^{2+} (3d^6)$ strong field (no unpaired e^-)

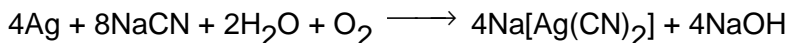


$[\text{Co}(\text{ox})_2(\text{H}_2\text{O})]^- = \text{Co}^{+5} (3d^4)$ (weak field) 4 unpaired e^-

$[\text{Ti}(\text{NH}_3)_6]^{3+} = \text{Ti}^{3+} (3d^1)$ (one unpaired e^-)

15.(B) Greater the extent of $d\pi - p\pi$ back bonding, smaller will be the bond order of CO bond in metal carbonyls. In $\text{Fe}(\text{CO})_5$, there is maximum number of valence shell electrons (d -electrons), greatest chances of $p\pi - d\pi$ back bonding, lowest bond order of CO bond.

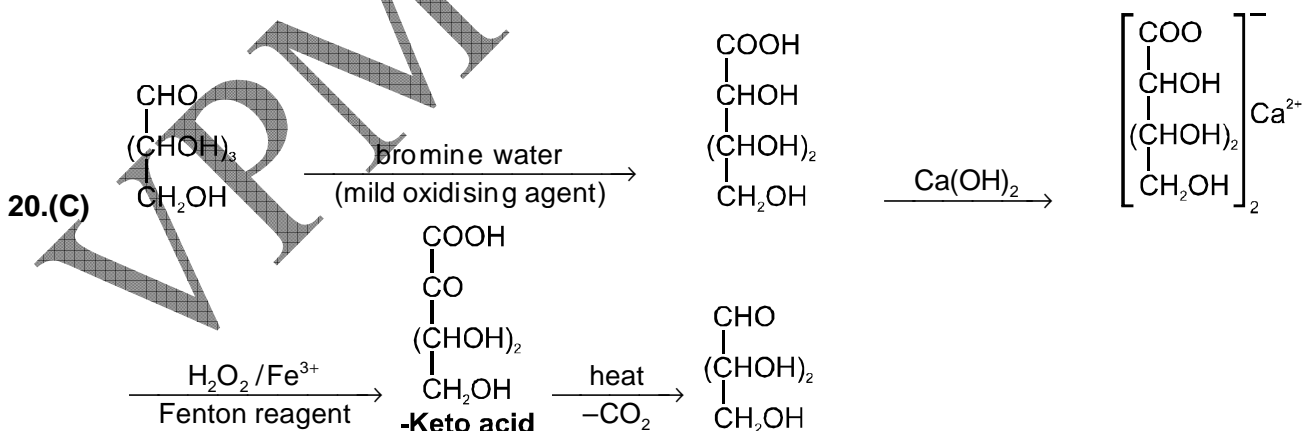
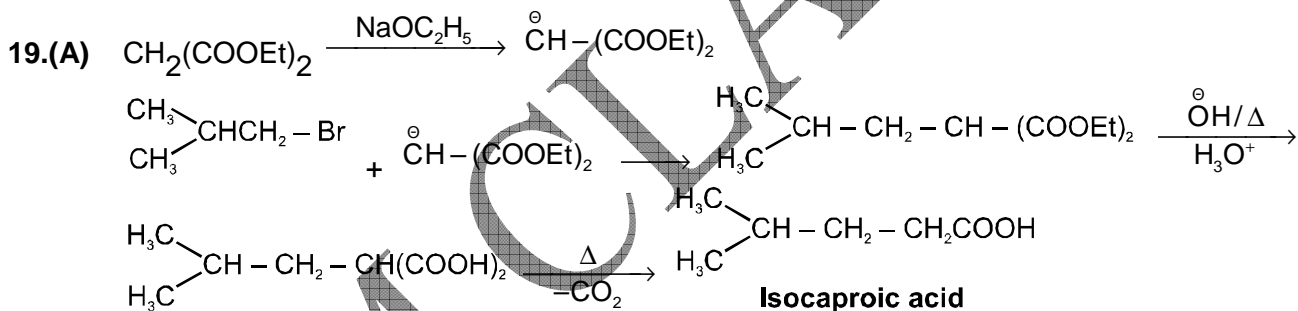
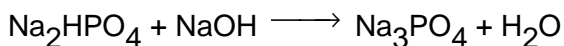
16.(B) A water soluble complex with silver and dilute aqueous solution of NaCN is $\text{Na}[\text{Ag}(\text{CN})_2]$. In the cyanide process, the native silver is crushed and treated with aqueous NaCN solution and aerated.

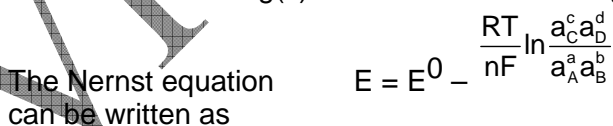
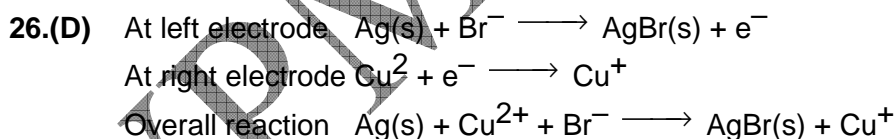
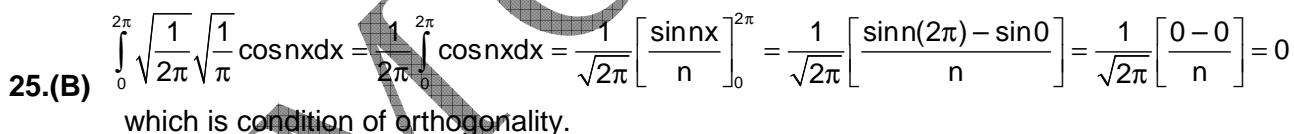
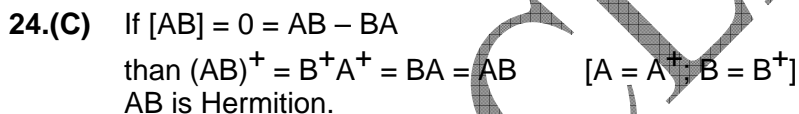
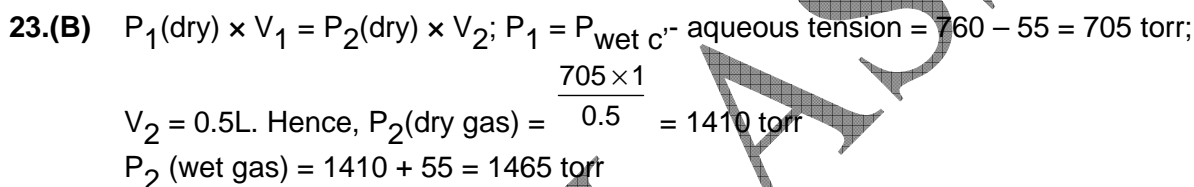
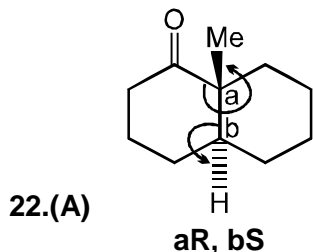
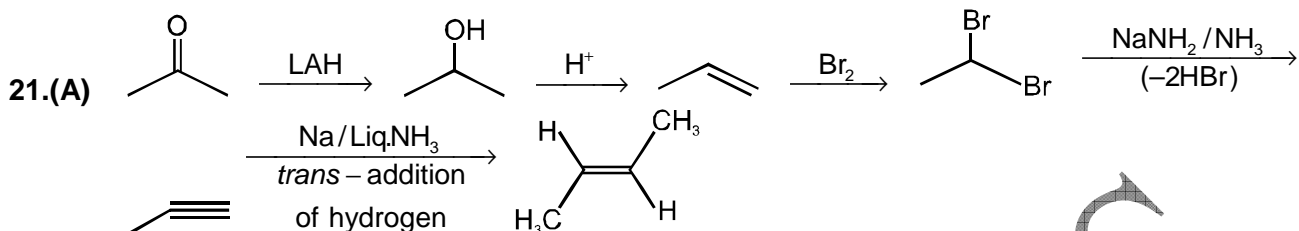


17.(A) $\text{MgSO}_4 + \text{NH}_4\text{OH} + \text{Na}_2\text{HPO}_4 \longrightarrow \text{Mg}(\text{NH}_4)\text{PO}_4 \downarrow$ **white** $+ \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$

18.(B) $\text{NaH}_2\text{PO}_3 + \text{NaOH} \longrightarrow \text{Na}_2\text{HPO}_3 + \text{H}_2\text{O}$

Na_2HPO_3 is normal salt and does not react any more with NaOH.





$$E = E^0 - \frac{(0.0591)}{(1)} \log \frac{a_{\text{Cu}^{2+}}}{a_{\text{Cu}^{2+}} a_{\text{Br}^-}}$$

$$\text{i.e. } 0.0565 = E^0 - (0.0591) \log \frac{0.36}{0.42 \times 0.32} = E^0 - 0.0253$$

$$E_0 = 0.0565 + 0.0253 = 0.818 \text{ V}$$

27.(A) $\bar{\nu} = R \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$; $n = 5, n' = 8$ for the 3rd line.

$$= 109677.76 \times \left(\frac{1}{5^2} - \frac{1}{8^2} \right) = 2673.39 \text{ cm}^{-1}$$

28.(B) $V_1 = \frac{RT}{p} = \frac{(0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})(1 \text{ mol})}{3 \text{ atm}} = 8.2 \text{ dm}^3$

$$V_2 = \frac{p_1 V_1}{p_2} = \frac{(3 \text{ atm})(8.2 \text{ dm}^3)}{(1.5 \text{ atm})} = 16.4 \text{ dm}^3$$

$$W = p_{\text{ex}} \Delta V = (1.5 \text{ atm})(16.4 - 8.2) \text{ dm}^3 = 12.3 \text{ atm dm}^3 = 1.246 \times 10^3 \text{ J}$$

Since work is done by the system so it is positive.

29.(C) From the slow step : rate = $k_2[A][B]$... (i)

From fast step : $K_e = \frac{[A]^2}{[A_2]}$ or $[A] = K_e^{1/2}[A_2]^{1/2}$... (ii)

From (i) and (ii) rate = $k_2 k_e^{1/2} [A_2]^{1/2} [B] = k [A_2]^{1/2} [B]$

30.(D) The vectors $3p\hat{i} + \hat{j} + q\hat{k}$ and $2p\hat{i} + 3\hat{j} + 6q\hat{k}$ are orthogonal.

$$\therefore (3p\hat{i} + \hat{j} + q\hat{k}) \cdot (2p\hat{i} + 3\hat{j} + 6q\hat{k}) = 0$$

$$\Rightarrow 6p^2 + 3 + 6q^2 = 0$$

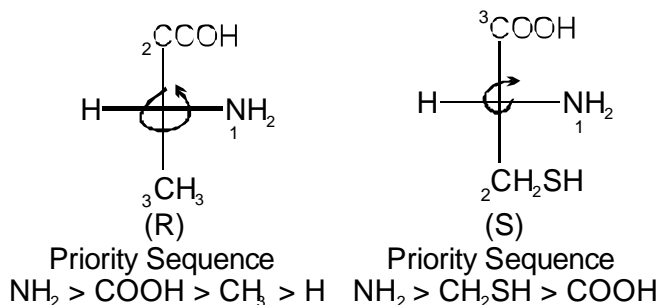
which is not possible because p^2 and q^2 are positive.

\therefore The given vectors can never be orthogonal.

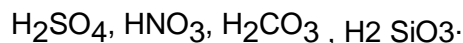
31.(C) According to MOT the bond order of N_2 is 3 whereas that of N_2^+ is 2.5. So the bond dissociation energy of N_2 will be greater than that of N_2^+ . Bond dissociation energy is directly proportional to bond order.

(B.O \propto BDE)

32. (B)

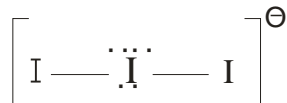


33. (A) These are the anhydrides of following acids:

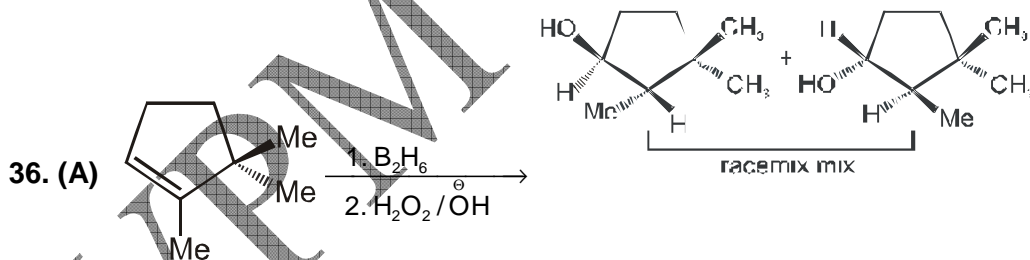


The acid strength order of these acid is H₂SO₄ > HNO₃ > H₂CO₃ > H₂SiO₃. The oxides also follow the same order.

34. (D) I₃⁻ — sp³d Hybridization with 3 lone pairs



35. (D) Arachno boranes have the general formula - B_nH_{n+6} with (n+ 3) electron pairs B₆H₁₂ is arachno borane.



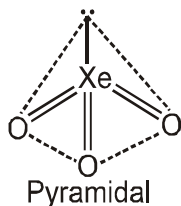
37.(D)

a	b	c
2	-3	-3
$\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{3}$
3	-2	-2

∴ Miller indices are $(3\bar{2}\bar{2})$.

38.(C) C_6H_5CHO and $C_6H_5-C(=O)-CH_3$ will differ in the absorption peaks due to aldehydic C – H ($2700-2800\text{ cm}^{-1}$) and sp^3 C – H stretch ($2860-2975\text{ cm}^{-1}$).

39. (A) XeO_3 has trigonal pyramidal shape .



$$40.(D) \quad EMF = EMF^0 + \frac{0.059}{6} \log \frac{[Au^{3+}]^2}{[Ni^{2+}]^3} = EMF^0 + \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3} = EMF^0 + \frac{0.059}{6} \log 10^4$$

$$= EMF^0 + \frac{0.059}{6} \times 4. \text{ Hence } EMF > EMF^0.$$

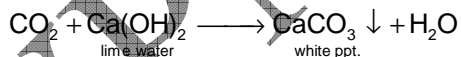
41. (X) is $NaHCO_3$ (molecular wt. = 84)

Reactions involved are given below :

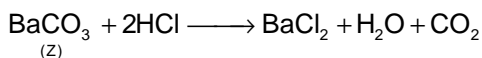
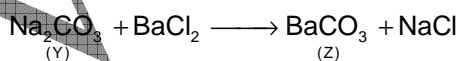


$$2 \times 84 = 168 \text{ g} \quad 106 \text{ g} \quad 44 \text{ g} \quad 18 \text{ g}$$

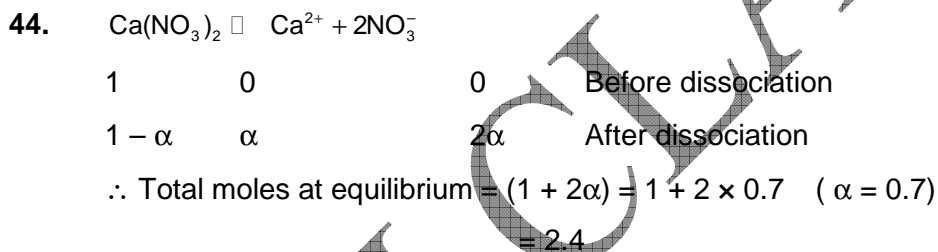
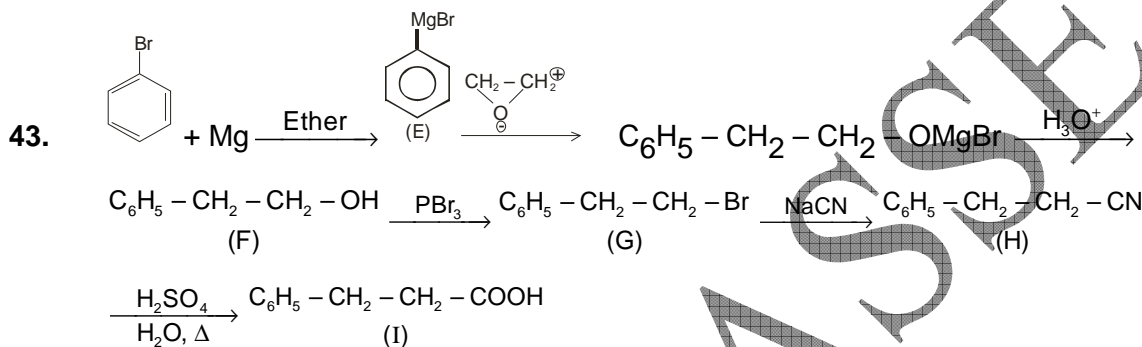
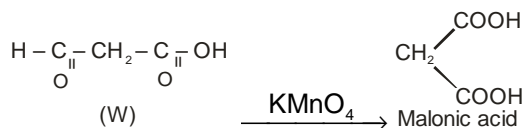
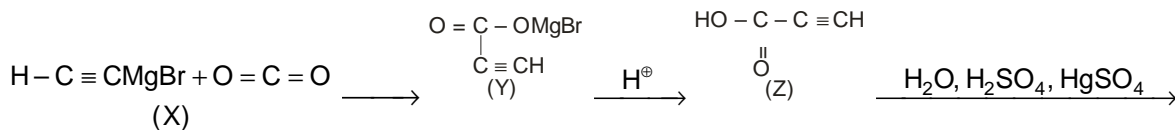
$$\approx 16.8 \text{ g} \quad 10.6 \text{ g} \quad 4.4 \text{ g} \quad 1.8 \text{ g}$$



$H_2O(g)$ is condensed to liquid water



42. $H-C \equiv C-H + CH_3MgBr \rightarrow HC \equiv CMgBr + CH_4$



For $\text{Ca}(\text{NO}_3)_2$: $\frac{m_{\text{nor}}}{m_{\text{exp}}} = 1 + 2\alpha$

$\therefore \frac{m_{\text{nor}}}{m_{\text{exp}}} = \frac{164}{1 + 2 \times 0.7} = \frac{164}{2.4} = 68.33$

Also at 100°C , $P_0 = 760$ mm, $w = 7$ g

$W = 100$ g

Raoult's Law

$\therefore \frac{P_0 - P_s}{P_s} = \frac{wM}{Wm}$

$$\text{Now, } \frac{P_o - P_s}{P_s} = \frac{7 \times 18}{68.33 \times 100} = 0.0184 \quad \text{or} \quad \frac{P_o}{P_s} - 1 = 0.0184$$

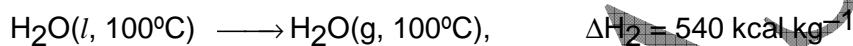
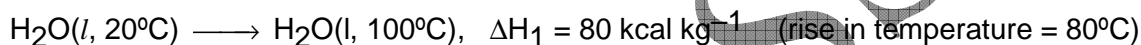
$$\therefore P_s = \frac{760}{1.0184} = 746.26 \text{ m}$$

45. $1.00 \text{ m}^3 \text{ at STP} = 1000 \text{ L} = \frac{1000}{22.4} \text{ mol}$

Enthalpy change due to burning of 1.00 m^3 ethylene = $-337 \times \frac{1000}{22.4} \text{ kcal}$

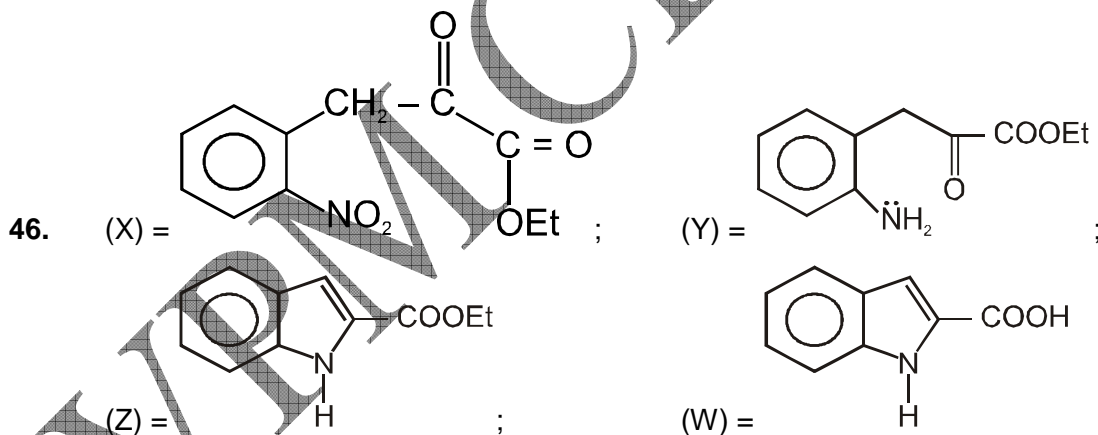
Due to 70% efficiency, useful heat is = $337 \times \frac{1000}{22.4} \times \frac{70}{100} \text{ kcal}$

$\text{H}_2\text{O}(l)$ is converted into $\text{H}_2\text{O}(g)$ in two stages



$$\Delta H(\text{Total}) = 620 \text{ kcal kg}^{-1}$$

thus, water converted into steam = $\frac{\text{heat evolved}}{\text{heat required}} = \frac{337 \times 1000}{22.4} \times \frac{70}{100} \times \frac{1}{620} = 16.98 \text{ kg}$



47. Total vapour-pressure of solution:

$$P_m = P_{\text{eth}}^o \times M.F._{\text{eth}} + P_{\text{meth}}^o \times M.F._{\text{meth}} = \underbrace{P_{\text{eth}}^o \times x_{\text{eth}}}_{P_{\text{eth}}} + \underbrace{P_{\text{meth}}^o \times x_{\text{meth}}}_{P_{\text{meth}}}$$

Given that:

$P_{\text{eth}}^{\circ} = 44.5 \text{ mm Hg}$, $p_{\text{meth}}^{\circ} = 88.7 \text{ mm Hg}$
wt. of ethanol = 60 g, wt. of methanol = 40 g

$$\therefore n_{\text{eth}} = \frac{60}{40} = 1.304 \quad (\text{mol. wt. of ethanol} = 40)$$

$$n_{\text{meth}} = \frac{40}{32} = 1.25 \quad (\text{mol. wt. of methanol} = 32)$$

$$x_{\text{eth}} = \frac{n_{\text{eth}}}{n_{\text{eth}} + n_{\text{meth}}} = \frac{1.304}{1.304 + 1.25} = \frac{1.304}{2.554} = 0.51$$

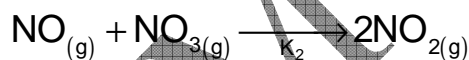
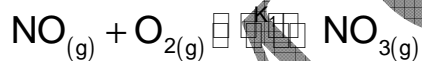
$$x_{\text{meth}} = \frac{n_{\text{meth}}}{n_{\text{meth}} + n_{\text{eth}}} = \frac{1.25}{2.554} = \mathbf{0.49}$$

$$\therefore P_m = 44.5 \times 0.51 + 88.7 \times 0.49 = 22.67 + 43.46 = 66.13 \text{ mm Hg}$$

$$\text{mole-fraction of methanol in vapour} = \frac{P_{\text{meth}}}{P_m} = \frac{43.46}{66.13} = \mathbf{0.66 \text{ mm Hg}}$$

48. (a) No, A collision among three molecules is not likely. The $[\text{NO}]^2$ term results because the slowest step in the mechanism depends on $[\text{NO}]$ and some other concentration term that is directly related to $[\text{NO}][\text{O}_2]$.

(b) The slowest step is the second step in the proposed reaction mechanism. Assuming that the first step is fast and has reached a state of equilibrium,



then the concentration of $\text{NO}_3(g)$ is related to the concentrations of $\text{NO}(g)$ and $\text{O}_2(g)$ by the equilibrium relation $K_1 = [\text{NO}_3]/[\text{NO}][\text{O}_2]$ or $[\text{NO}_3] = K_1[\text{NO}][\text{O}_2]$. The rate law for the reaction, as derived from the slowest step, is $\Delta[\text{O}_2]/\Delta t = k_2[\text{NO}][\text{NO}_3] = K_2[\text{NO}]$

$$K_1[\text{NO}][\text{O}_2] = k_1 k_2 [\text{NO}]^2 [\text{O}_2] = k[\text{NO}_2]^2 [\text{O}_2].$$

(c) Both steps are bimolecular.

49. At temperatures ($0 < T < 20 \text{ K}$), $C_p = C_v = aT^3$

[Debye's T^3 law]

$$a = C_v / T^3 = 3.04 \text{ JK}^{-1} \text{ mol}^{-1} / (20\text{K})^3 = 38.03 \times 10^{-5} \text{ JK}^{-4} \text{ mol}^{-1}$$

Hence, $C_p = aT^3 = (38.3 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-4}) T^3$

From Eq.14, $dS = (C_p/T)dT = 38.03 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-4} T^2 dT$

Or $S_{20} - S_0 = 38.03 \times 10^{-5} \text{ JK}^{-4} \text{ mol}^{-1} (20\text{K})^3 / 3$

Or $S_{20} = 1.01 \text{ JK}^{-1} \text{ mol}^{-1} \quad [\because S_0 = 0]$

50. A/C to langmuir isotherm

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

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

Let $\theta = \frac{v}{v_{\text{mono}}}$

Where v_{mono} is the volume corresponding to complete coverage

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

Multiplying throughout by $\frac{p}{v_{\text{mono}}}$

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

$$y = mx + C$$

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