Pre Nurture & Career Foundation Division															
	For Class 6th to 10th, Olympiads & Board														
	ANSWER KEY (Paper Code : 34)														
NATIONAL STANDARD EXAMINATION in CHEMISTRY															
NSEC-2023 [24-11-2024]															
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	b	а	а	с	с	с	d	а	b	с	d	b	с	b	с
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	с	a,b,c,d	d	d	с	с	b	d	а	b	b	b	b	с	а
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	с	с	d	а	а	b,d	b	d	a	d	b	b	с	d	с
Que.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
Ans.	c	b	a,b	a,b,c	b,c	a,c,d	a,c	a,d	b,c	a,b,d	b,d	b,c,d	a,b,c,d	b,d	b,d
NA = Options are Not Correct															
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## NSEC-2024 (NSEC STAGE-I)

Date of examination : 24th Nov, 2024

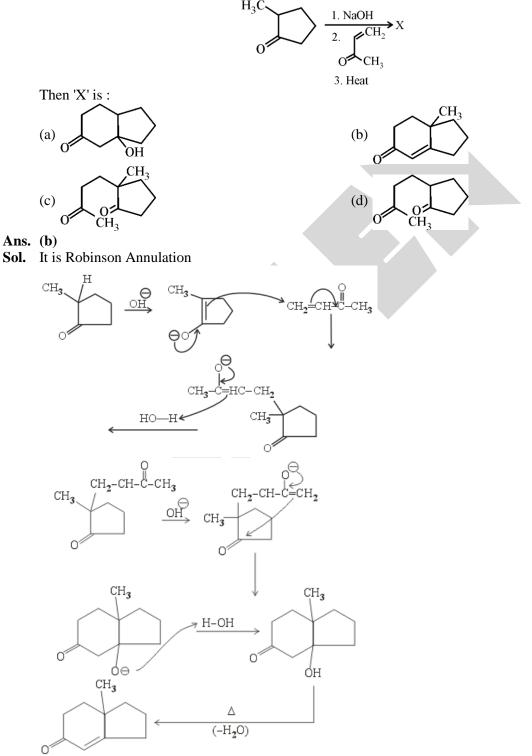
Date: 24/11/2024

### PAPER CODE - 34

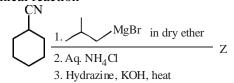
### Max. Marks: 00

# Time allowed: 3 hours PAPER WITH SOLUTIONS

When 2-Methylcyclopentanone is treated with but-3-en-2-one under alkaline condition followed by heating gives the major product 'X'.



2. Consider the following chemical reaction

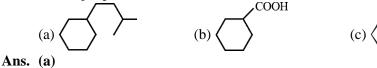


CHO

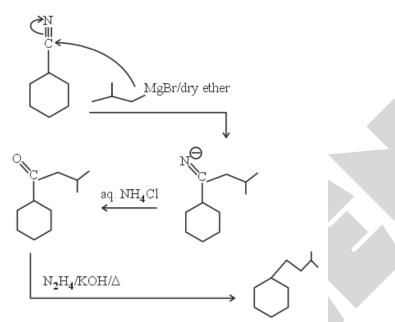
CH<sub>2</sub>OH

(d)

The major product 'Z' formed in the reaction is :



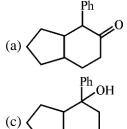
Sol.

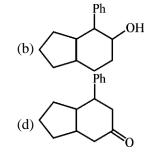


3. Consider the set of the following reactions. Ph

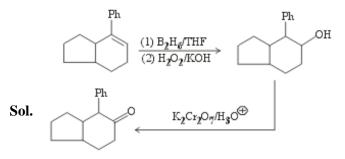
$$\underbrace{\xrightarrow{B_2H_6, THF}}_{H_2O_2, KOH} P \xrightarrow{K_2Cr_2O_7, H_3O^+} Q$$

The final major product 'Q' is :

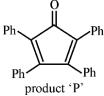




Ans. (a)



4. The following product 'P' given below is obtained by Aldol condensation of ...



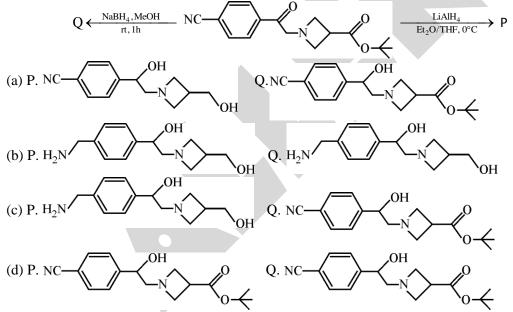
- (a) 2 moles of dibenzyl ketone, (PhCH<sub>2</sub>)<sub>2</sub>CO
- (b) 1 mole of dibenzyl ketone, (PhCH<sub>2</sub>)<sub>2</sub>CO and 1 mole of acetone CH<sub>3</sub>COCH<sub>3</sub>
- (c) 1 mole of dibenzyl ketone,  $(PhCH_2)_2CO$  and 1 mole of benzil (PhCOCOPh)
- (d) 2 moles of benzophenone, PhCOPh.

Ans. (c)

Sol.



5. The structures of 'P' and 'Q' formed in the following reactions are :



Ans. (c)

Sol. NaBH<sub>4</sub> cannot reduce cyanide and ester, while LiAlH<sub>4</sub> reduces them both.

6. An amount of 0.45 g of an organic compound X containing C, H and N on combustion produces 1.1 g of CO<sub>2</sub> and 0.3 g of water. Empirical formula of X is : (a) CH<sub>2</sub>N<sub>2</sub> (b) C<sub>2</sub>H<sub>3</sub>N (c) C<sub>3</sub>H<sub>4</sub>N (d) C<sub>2</sub>H<sub>5</sub>N Ans. (c) Sol. % of C =  $\frac{12}{44} \times \frac{1.1}{0.45} \times 100 = 66.67\%$ 

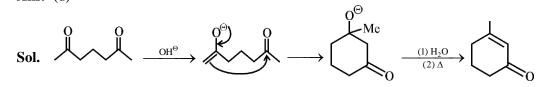
% of H = 
$$\frac{2}{18} \times \frac{0.3}{0.45} \times 100 = 7.41\%$$
  
% of N = 100 - (66.67 + 7.41) = 25.92%  
Now, N<sub>C</sub> : N<sub>H</sub> : N<sub>N</sub> =  $\frac{66.67}{12} : \frac{7.41}{1} : \frac{25.92}{14} \approx 3 : 4 : 1$   
Hence, empirical formula of X = C<sub>3</sub>H<sub>4</sub>N

Heptane-2, 6-dione was treated with aqueous alkali and heated. The major product obtained is : 7. (a) 2, 3-dimethylcyclohex-1-ene-2-one (b) 2, 3-dimethylcyclohex-1-ene-3-one

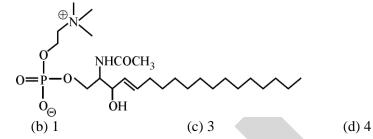
(c) 2, 3-dimethylcyclohex-2-ene-1-one

Ans. (d)

(d) 3-methylcyclohex-2-enone

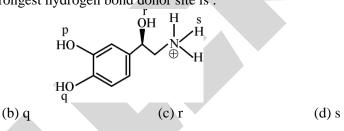


8. The number of chiral carbon(s) in Sphingomyelin, an important constituent of a class of lipids with the following structure is :



(a) 2 Ans. (a)

- The carbon atoms containing –NHCOCH<sub>3</sub> and –OH groups in the diagram are chiral. Sol.
- 9. In the following ion the strongest hydrogen bond donor site is :



(a) p Ans. (b)

- Strongest donor contains the most acidic hydrogen. Sol. ∴ "Q" has most acidic hydrogen.
- The double bond equivalents for the compounds with the following molecular formulae are 10. respectively :

	(i) $C_{13}H_9BrO$	(ii) $C_3H_7N$	(iii) $C_{10}H_7Cl$	
	(a) 1, 5, 6	(b) 5, 6, 1	(c) 9, 1, 7	(d) 7, 9, 1
Ans.	(c)			
Sol.	$C_{13}H_9BrO \rightarrow DOU = 9$	9		

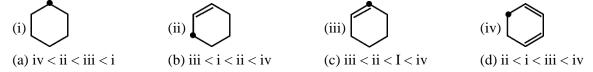
- So  $C_3H_7N \rightarrow DOU = 1$  $C_{10}H_7Cl \rightarrow DOU = 7$
- 11. Match the following in which acetaldehyde is converted into different compounds (Column 1) using specific reagents (Column 2)

	Column 1	Column 2		
i.	$CH_3CH = CHCHO$	1.	EtMgI in dry ether, $H_3O^+$ , acid dichromate	
ii.	CH <sub>3</sub> COCl	2.	Dilute NaOH/Heat	
iii.	CHI <sub>3</sub>	3.	Acid dichromate, PCl <sub>5</sub>	
iv.	CH <sub>3</sub> COEt	4.	I <sub>2</sub> , NaOH	
( ) •	1 2 4 2 0 1	$\langle \rangle$		

(a) i-1, ii-3, iii-4, iv-2 (b) i-4, ii-3, iii-2, iv-1 (c) i-2, ii-4, iii-1, iv-3 (d) i-2, ii-3, iii-4, iv-1 Ans. (d)

- Sol. (i) Self aldol
  - (ii) Oxidation, followed by reaction with PCl<sub>5</sub>
  - (iii) Iodoform reaction
  - (iv) Nucleophilic addition of Et Mg X, followed by oxidation.

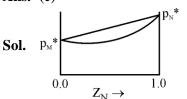
12. The increasing order of stability of the following free radicals is :



Ans. (b)

- Sol. (iv) Maximum conjugation.
  - (ii) Less conjugation.
  - (i)  $4\alpha H$
  - (ii) Radical on more electronegative carbon.
- 13. A closed vessel with rigid walls contains 1.0 mol of component M (vapour pressure( $p_M^*$ ); 0.9 mol liquid and 0.1 mol vapor, 0.1 mol of component N (vapour pressure  $P_N^*$ ) is added slowly to maintain equilibrium conditions. Assume M and N form an ideal solution. The total pressure at the end of the addition will :
  - (a) decrease if  $p_M^* < p_N^*$
  - (b) decrease irrespective of relation between  $p_M^*$  and  $p_N^*$
  - (c) increase if  $p_M^* < p_N^*$
  - (d) increase irrespective of relation between  $p_M^*$  and  $p_N^*$





On adding N, whether liquid or vapour, the vapour pressure of solution increases, if  $P_M^* < P_N^*$ .

14. A scuba diver accidentally surfaces from a depth of 100 feet in water (pressure = 4 atm). The solubility of nitrogen from air (78% N<sub>2</sub> in air) in water in standard conditions is 15 mg L<sup>-1</sup> at 37°C. The volume of N<sub>2</sub> gas released into the bloodstream of the diver from each litre of blood is : (a) 14 mL (b) 41 mL (c) 55 mL (d) 12 mL

Ans. (b)

Sol. Solubility at 1 atm = 15 mg L<sup>-1</sup>  $\therefore$  Solubility at 4 atm = 60 mg L<sup>-1</sup> Moles of N<sub>2</sub> gas dissolved per litre =  $(60 - 15) \times 10^{-3} / 28$  $\therefore$  Volume of N<sub>2</sub> gas dissolved =  $\frac{45 \times 10^{-3}}{28} \times 0.082 \times 310}{28}$ 

$$= 40.85 \times 10^{-3} L \approx 41 \text{ ml}.$$

15. A 35 degree drop in temperature from 25°C causes a 8.2 fold decrease in the rate of a first order reaction. If the half-life of the reaction is 3.2 h, what will be the half-life at a temperature of -10°C ?
(a) 12.8 h
(b) 19.8 h
(c) 26.2 h
(d) 23.4 min.

Ans. (c)

Sol.  $\frac{K_{(-10^{\circ}C)}}{K_{25^{\circ}C}} = \frac{(t_{1/2})_{25^{\circ}C}}{(t_{1/2})_{(-10^{\circ}C)}} = \frac{1}{8.2}$  $\therefore (t_{1/2})_{-10^{\circ}C} = 8.2 \times 3.2 = 26.24 \text{ hr.}$  16. An ideal-gas reaction equilibrium is represented as  $A + B \implies C + D$ . Considering, the fact that all components are ideal and that only A and B are present initially, which of the following options is ALWAYS true at equilibrium ? 'N' is the number of moles of the species. (b)  $N_{C} + N_{D} = N_{A} + N_{B}$  (c)  $N_{C} = N_{D}$ (a)  $N_{C} = N_{A}$ (d)  $N_A = N_B$ 

Ans. (c) Sol.  $B \implies C + D$ Α

b mole 0 0 t = 0 a mole  $t = t_{eq}$  (a-x)mole (b-x) mole x mole x mole  $\therefore$  N<sub>C</sub> = N<sub>D</sub>

17. Which of the following statements is correct?

> (a) The addition of neon to a gas-phase reaction mixture at equilibrium at constant T and constant V does not alter the equilibrium.

> (b) For a reversible reaction in a closed system with constant T and constant P if  $\left(\frac{\partial G}{\partial \xi}\right)_{n=0} > 0$ , the

reaction proceeds in the reverse direction. Here ' $\xi$ ' is the extent of the reaction.

(c) Complete dissociation of a weak electrolyte takes place in the limit of infinite dilution in aqueous solution.

- (d) The standard state of a species is always a pure substance.
- **Ans.** (a,b,c,d)
- Sol. (A) Equilibrium is not disturbed on adding non-reactive gas at constant T and V.
  - (B) If  $\left(\frac{\partial G}{\partial E}\right)_{T,P} > 0$ , reaction is spontaneous in backward direction.
  - (C) When  $C \rightarrow 0, \alpha \rightarrow 1$

(D) Standard state of any species is the pure substance at 1.0 bar pressure and any specified temperature.

18. Consider the following statements about the given mechanism :

 $A + B \rightarrow C + D$  $2C \rightarrow F$  $F + B \rightarrow 2A + G$ (i) The overall reaction is  $3B \rightarrow 2D + G$ (ii) A is a catalyst and B is a reactant. (iii) C and F are intermediates. (iv) D and G are products The correct set of statements is : (b) (iii) and (iv) only (a) (i) and (ii) only (c) (ii), (iii) and (iv) only (d) All (i), (ii), (iii) and (iv) Ans. (d) Sol.  $[A + B \rightarrow C + D] \times 2$  $2C \rightarrow F$  $F + B \rightarrow 2A + G$ 

Net reaction :  $3B \rightarrow 2D + G$ 

As A is reacted in step I and re-generated in further steps, A is catalyst. As C and F are not appearing in the net reaction, they are intermediates.

For one mole of a van der Waal gas with b = 0, the plot of PV versus 1/V at 298 K gives an intercept 19. of 24.4 L atm K mol-1 and slope of  $-2.5 L^2$  atm mol<sup>-2</sup>. The value of the van der Waal constant a is : (a)  $12.5 \text{ L}^2 \text{ atm mol}^{-2}$  (b)  $5.0 \text{ L}^2 \text{ atm mol}^{-2}$ (c)  $4.5 L^2$  atm mol<sup>-2</sup> (d)  $2.5 L^2$  atm mol<sup>-2</sup>

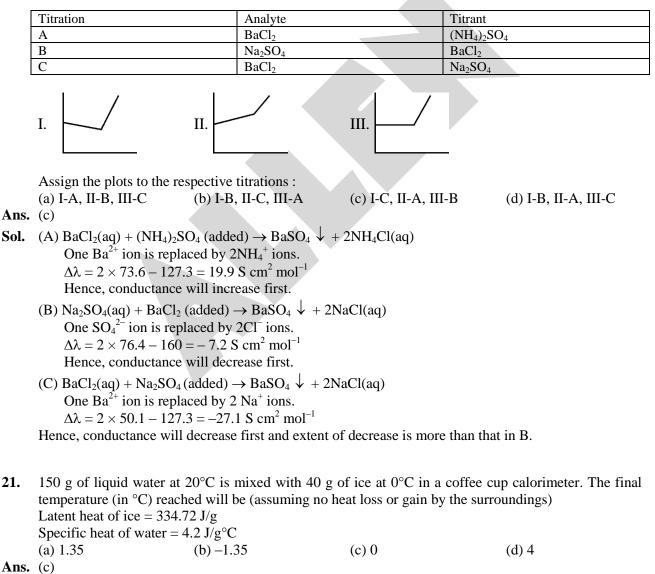
Ans. (d)

**Sol.**  $\left(P + \frac{a}{V^2}\right) \cdot V = RT$ 

or,  $PV = RT - \frac{a}{V}$ Slope of (PV) vs  $\left(\frac{1}{V}\right)$  graph is (-a) and from question it is (-2.5 L<sup>2</sup> atm mol<sup>-2</sup>). Hence, a = 2.5 L<sup>2</sup> atm mol<sup>-2</sup>.

20. The following three plots show the variation of conductance with mL of titrant added for three titrations of aqueous solutions of Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, BaCl<sub>2</sub>
 Given : Molar ionic conductivities in S cm<sup>2</sup> mol<sup>-1</sup> are

Ba <sup>2+</sup>	Cl	Na <sup>+</sup>	$SO_4^{2-}$	$\mathrm{NH_4}^+$
127.3	76.4	50.1	160	73.6



Sol. Heat gained in complete melting of ice =  $mL = 40 \times 334.72 = 13388.8 \text{ J}$ Heat lost in complete cooling water upto 0°C = m.s.  $\Delta T = 150 \times 4.2 \times 20 = 12600 \text{ J} < 13388.8 \text{ J}$ hence, ice will not melt completely and the final temperature of system will remain 0°C. 22. A chemical reaction,  $X(g) + Y(g) \rightarrow Z(g)$  has following mechanism :

 $X(g) + S(s) \xrightarrow{k_1 \ k_2} [X - S] (s)$  $[X - S] (s) + Y(g) \xrightarrow{k_3 \ k_4} Z(g) + S(s); [where (S) is solid catalyst]$ The overall equilibrium constant for above reaction can be represented as : 1-1 1-2 1.1 1.2

(a) 
$$K = \frac{k1.k2}{k3.k4}$$
  
(b)  $K = \frac{k1.k3}{k2.k4}$   
(c)  $K = \frac{k4.k1}{k2.k3}$   
(d)  $K = \frac{k4.k2}{k3.k1}$ 

Ans. (b)

**Sol.** Overall  $K = K_{eq(1)} \cdot K_{eq(2)} = \frac{K_1}{K_2} \cdot \frac{K_3}{K_2}$ 

23. Given below is a galvanic cell  $Cu(s) | Cu^{2+}(aq) (x M) || Ag+(aq) (y M) | Ag(s)$ The possible condition for the galvanic cell to develop emf of 0.5 V is :  $[Given:\,E^{\rm o}_{Cu^{2+}/Cu}$  = 0.34 V and  $\,E^{\rm o}_{Ag^+/Ag}$  = 0.8 V] (a) x = 0.015 and y = 0.3(b) x = 0.05 and y = 0.25(c) x = 0.04 and y = 0.2(d) x = 0.011 and y = 0.5Ans. (d)

**Sol.** 
$$E_{cell}^{o} = E_{Ag^{+}/Ag}^{o} - E_{Cu^{2+}/Cu}^{o} = 0.80 - 0.34 = 0.46 \text{ V}$$

Net cell reaction :  $Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Aq(s)$   $0.059 \text{ Let } [Cu^{2+}]$ 

У<sup>2</sup>

Now, 
$$E_{cell} = E_{cell}^{o} - \frac{0.059}{n} \cdot \log \frac{[Cu^{2+}]}{[Ag^{+}]^{2}}$$
  
or,  $0.50 = 0.46 - \frac{0.059}{n} \cdot \log \frac{x}{100}$ 

From given options : x = 0.011, y = 0.5

2

If 5A current is passed for a hour through one dm<sup>3</sup> 0.5 M aqueous solution of sodium acetate, then the 24. amount of ethane produced will be :

Ans. (a)

Sol.  ${}^{2CH_3 - C - O^-} \rightarrow CH_3 - CH_3 + 2CO_2 + 2e 2 \times 96500 \text{ C}$ 30 gm

 $\therefore 2 \times 96500$  C charge will produce 30 gm C<sub>2</sub>H<sub>6</sub>

 $\therefore 5 \times 3600 \text{ C charge will produce} = \frac{30}{2 \times 96500} \times 5 \times 3600 = 2.79 \text{ gm}.$ 

**25.** The results obtained when the finely divided metal powders of P, Q, R and S added to the aqueous solutions of different metal nitrates are given below :

Metal	Silver Nitrate	Lead Nitrate	Nickel Nitrate	Zinc Nitrate
Р	$\checkmark$	$\checkmark$	$\checkmark$	×
Q	$\checkmark$	$\checkmark$	✓	✓
R	$\checkmark$	$\checkmark$	×	×
S	✓	×	×	×

Displacement =  $\checkmark$ , No reaction =  $\texttt{\times}$ .

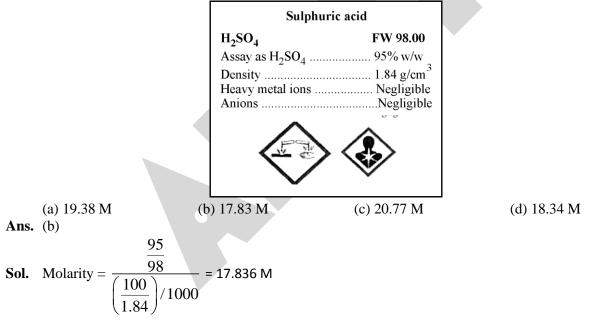
 $[Given: E^{\rm o}_{Ag^+/Ag} = 0.80 \text{ V}, \ E^{\rm o}_{Zn^{2+}/Zn} = -0.76, \ E^{\rm o}_{Ni^{2+}/Ni} = -0.25, \ E^{\rm o}_{Pb^{2+}/Pb} = -0.13 \text{ V}]$ 

If these elements are to be arranged as per their positions in the electrochemical series, then which of the following will represent the above set of observations ?

(a) P > Q > R > S (b) S > R > P > Q (c) Q > P > R > S (d) S > R > Q > PAns. (b)

Sol. Order of oxidation potential of metals : Q > P > R > SHence, order of reduction potential of metals : Q < P < R < SIn NCERT, electrochemical series is in the order of decreasing SRP values and hence, the order is S > R > P > Q.

**26.** The molarity of the commercially available concentrated sulphuric acid solution with label on the bottle is as shown below is :



**27.** Oxide ions with ions of metals A and B together, form a crystal. The oxide ions get organized into a cubic closed packed (ccp) lattice. In the oxide lattice, the metal ion A occupy 25% of the octahedral voids and the metal ion B occupies 50% of the tetrahedral voids. Oxidation states of A and B respectively are :

(a) +3, +1 (b) +4, +1 (c) +1, +3 (d) +2, +4 Ans. (b) Sol.  $Z_{0^{2-}} = 4$   $Z_{A^{n+}} = 4 \times \frac{25}{100} = 1$  $Z_{B^{m+}} = 8 \times \frac{50}{100} = 4$ 

As the oxide will be neutral, the possible oxidation state of A is +4 and B is +1.

### **28.** Consider the statements :

(i) Energy of the electron in the fourth orbit of  $He^+$  ion is less than the energy of the electron in the fourth orbit of hydrogen atom.

(ii) Radius of the first orbit of  $\text{He}^+$  ion is 0.529 Å.

(iii) In the Lyman series as the energy liberated during the transition increases then the distance between the spectral lines goes on decreasing.

(iv) If the radius of the 2<sup>nd</sup> orbit of Li<sup>2+</sup> is x, the expected radius of the 3<sup>rd</sup> orbit of Be<sup>3+</sup> is  $\frac{9}{4}$  x.

(v) In hydrogen atom, 3p and 3d-orbitals are not degenerate orbitals. The correct set of statements is :

(a) (i) and (ii) (b) (i) and (iii) (c) (ii), (iii) and (iv) (d) (i), (iii) and (v) **Ans.** (b)

**Sol.** (i)  $E_{n,z} = -13.6 \times \frac{z^2}{n^2}$  eV

:: 
$$E_4$$
,  $_{He^+} < E_{4,H}$   
(ii)  $r_{1,He^+} = 0.529 \times \frac{1^2}{2} = 0.2645 \text{ Å}$ 

(iii) On increasing the orbit number, the energy difference decreases and hence, spectral lines come closer.

(iv) 
$$r_{n,z} \propto \frac{n^2}{z}$$
  
$$\frac{r_{3,Be^{3+}}}{r_{2,Li^{2+}}} = \frac{\left(\frac{3^2}{4}\right)}{\left(\frac{2^2}{3}\right)} = \frac{27}{16}$$
$$\therefore r_{3,Be^{3+}} = \frac{27}{16}x$$

(v) In hydrogen atom, energy of electron depends only on 'n' and hence 3p and 3d are degenerate orbitals.

29.	The mixture of $Al(OH)_3$ and $Fe(OH)_3$ can be separated by :				
	(i) leaching method	(ii) froth floatation method			
	(iii) gravity separation method	(iv) magnetic separation method			

(a) (i) and (ii) only **Ans.** (c)

**Sol.** Leaching and magnetic separation can be used for  $Al(OH)_3$  and  $Fe(OH)_3$  respectively.

(b) (ii) and (iii) only

**30.** The anions giving white precipitate completely soluble in concentrated hydrochloric acid with barium chloride solution are :

(i) sulphite(ii) carbonate(iii) sulphate(iv) nitrate(a) (i) and (ii) only(b) (ii) and (iii) only(c) (i) and (iv) only(d) (i), (iii) and (iv)only(a)(b) (ii) and (iii) only(c) (i) and (iv) only(d) (i), (iii) and (iv)

(c) (i) and (iv) only

(d) (iii) and (iv) only

Sol.  $Ba^{+2} + SO_3^{-2} \rightarrow BaSO_3 \downarrow$  [White ppt. soluble in conc. HCl]  $Ba^{+2} + CO_3^{-2} \rightarrow BaCO_3 \downarrow$  [White ppt. soluble in conc. HCl]  $Ba^{+2} + SO_4^{-2} \rightarrow BaSO_4 \downarrow$  [White ppt. insoluble in conc. HCl]  $Ba^{+2} + NO_3^{-2} \rightarrow Ba(NO_3)_2$  [Soluble compound]

- **31.** The substituted silanes which can produce dimeric and cyclic trimeric silicone polymers, respectively on hydrolysis are :
  - 1.  $RSiCl_3$ 2.  $R_2SiCl_2$ 3.  $R_3SiCl$ (a) 1, 2(b) 1, 3(c) 3, 2(d) 2, 3

Ans. (c)

- **Sol.** R<sub>3</sub>SiCl on hydrolysis can produce dimeric silicones, while R<sub>2</sub>SiCl<sub>2</sub> on hydrolysis will give cyclic trimeric silicone polymers.
- **32.** Identify the correct pair of species with the correct description.
  - (a)  $CH_4 \rightarrow CH_3$ -change in both hybridization and shape.
  - (b)  $NH_3 \rightarrow NH_4^+$ -no change in shape and change in hybridization
  - (c)  $BF_3 \rightarrow BF_4^-$  -change in both hybridization and shape.
  - (d)  $H_2O \rightarrow H_3O^+$  -no change in hybridization as well as shape.

### Ans. (c)

- **Sol.**  $BF_3 \Rightarrow sp^2$  hybridized with trigonal planar shape.
  - $BF_4^{\Theta} \Rightarrow sp^3$  hybridized with tetrahedral shape.
- **33.** A student mixed three sodium salts accidently. To identify these salts, some tests were performed and found that.

(i) When chromyl chloride test was performed, mixture of colored gases released and NaOH solution turned yellow and gave positive test.

(ii) Brown ring test was positive but brown coloured gas was not intensified on adding copper turnings on heating the mixture with conc.  $H_2SO_4$ .

(iii) Aqueous solution of the mixture was treated with  $CHCl_3$  and chlorine water. From this chloroform layer  $CHCl_3$  test was performed. A violet organic layer was first visible then on more addition of concentrated HNO<sub>3</sub>, it changed to orange yellow. The observations indicate the presence of (a) chloride, bromide and iodide (b) nitrate, bromide and iodide

(c) fluoride, nitrate and iodide

(d) chloride, nitrite and iodide

Ans. (d)

- **Sol.** Among the observations :
  - (i) Since chromyl test is coming positive, it suggests anion can be chloride ion.

(ii) Brown ring test is positive, but intense brown fumes not appearing on addition of Cu turnings suggests the anion can be nitrite.

(iii) Violet layer in layer test suggests anion can be iodide.

34.	Total number of stereoisomers shown by the complex $[W(CO)_4 \{P(OR)_3\}SR']$						
	(where $R = -C_6H_5$ ; $R' = -CH_3$ )						
	(a) Two	(b) One	(c) Three	(d) Four			
<b>A</b>	(-)						

Ans. (a)

- 35. A, B and C are three complexes of chromium (III) with empirical formula H<sub>12</sub>O<sub>6</sub>Cl<sub>3</sub>Cr. All the three complexes have water and chloride ions are ligands. When subjected to heating at 200°C the mass of A was found to be constant, while that of B suffered a loss of 6.7%/ When 2.66 g of C was treated with AgNO<sub>3</sub> it gave 1.43 g of AgCl. The complexes B and C are respectively :

  [Cr(H<sub>2</sub>O)<sub>6</sub>Cl<sub>3</sub>]
  [Cr(H<sub>2</sub>O)<sub>6</sub>Cl]Cl<sub>3</sub>
  [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>.H<sub>2</sub>O
  [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl.2H<sub>2</sub>O
  [Cr(H<sub>2</sub>O)<sub>3</sub>Cl<sub>3</sub>].3H<sub>2</sub>O
  - (a) 3, 4 (b) 3, 5 (c) 1, 2 (d) 2, 5

Ans. (a)

**Sol.** In complex B, loss in weight is 6.7%, which is appx. 18 g, hence the compound should be  $[Cr(H_2O)_5Cl]Cl_2.H_2O$ .

In complex C, since the amount of ppt. (AgCl) is 0.01 mole, the complex should be  $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ 

Sol. The compound  $[W(CO)_4]P(OR)_3]SR'$  will have 2 geometrical isomers both optically inactive.

**36.** 126 g oxalic acid  $(H_2C_2O_4.2H_2O)$  under acidic condition will be oxidized by :

	(i) $\frac{1}{3}$ mole of K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	(ii) $\frac{5}{2}$ mol K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	(iii) $\frac{1}{3}$ mol KMnO <sub>4</sub>	(iv) $\frac{5}{2}$ mol KMnO <sub>4</sub>
Ans.	(a) i and iii only (b,d)	(b) i and iv only	(c) ii and iii only	(d) ii and iv only

**Sol.**  $n_{eq}$  of oxalic acid =  $\frac{126}{63} = 2$ 

(i) 
$$n_{eq} = \frac{1}{3} \times 6 = 2$$

- (ii)  $n_{eq} = \frac{5}{2} \times 6 = 15 > 2$
- (iii)  $n_{eq} = \frac{1}{3} \times 5 = 1.67 < 2$ (iv)  $n_{eq} = \frac{5}{2} \times 5 = 12.5 > 2$
- **37.** A carbonyl complex of Iridium (electronic configuration- [Xe]  $4f^{14} 5d^7 6s^2$ ) with the formula IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> is known as Vaska's complex. Which of the following ligand substitution/s will decrease the triple bond character of CO in Vaska's complex?
  - (a) Both PPh<sub>3</sub> by PMe<sub>3</sub>

(c)  $Cl^{-}$  by  $PF_3$ 

(b) Cl<sup>-</sup> by CH<sub>3</sub><sup>-</sup>
(d) Both PPh<sub>3</sub> by P(CH<sub>2</sub>Cl)<sub>3</sub>

Ans. (b)

- Sol.  $CH_3^{\Theta}$  will increase electron density on metal thereby weakening the carbon oxygen bond strength.
- **38.** A water sample is analysed and found to have concentration of  $Zn = 5.0 \text{ g m}^{-3}$ ,  $Fe = 0.5 \mu \text{g mL}^{-1}$ , Mn = 0.05 ppm and Cd = 0.005 ppb. The maximum prescribed concentration of metals in drinking water in mg dm<sup>-3</sup> is Zn = 5.0, Fe = 0.2, Mn = 0.05 and Cd = 0.005. Identify the correct statement about the sample of water.
  - (a) The water sample is having excess of Zn than the maximum prescribed concentration.

(b) The water sample is having lower concentration of Mn and Cd than the maximum prescribed concentration.

- (c) The water sample is potable (suitable for drinking)
- (d) The concentration of Fe is 0.5 ppm.

Ans. (d)

Sol.  $Zn = 5 g/m^3$   $10^3 L H_2O \rightarrow 5g$   $1 L \rightarrow 5 \times 10^{-3} g$  $1 dm^3 \rightarrow 5 mg$ 

 $\begin{array}{l} Mn = 0.05 \mbox{ ppm} \\ 10^6 \mbox{ g } H_2 O \rightarrow 0.05 \mbox{ g} \\ 10^6 \mbox{ mL } H_2 O \rightarrow 50 \mbox{ mg} \\ 10^3 \mbox{ mL } \rightarrow 0.05 \mbox{ mg} \\ (1 \mbox{ dm}^3) \end{array}$ 

$$\label{eq:Fe} \begin{split} Fe &= 0.5 \ \mu\text{g/mL} \\ 1\text{mL} \rightarrow 0.5 \times 10^{-6} \,\text{g} \\ 10^6 \ \text{mL} \rightarrow 0.5 \ \text{g} \\ 0.5 \ \text{ppm} \end{split}$$

```
\begin{array}{l} Cd = 0.005 \mbox{ ppb.} \\ 10^9 \mbox{ g } H_2O \rightarrow 0.005 \mbox{ g} \\ 10^9 \mbox{ mL } H_2O \rightarrow 5 \mbox{ mg} \\ 10^3 \mbox{ mL } \rightarrow 5 \times 10^{-6} \mbox{ mg} \\ (1 \mbox{ dm}^3) \end{array}
```

**39.** In the following reaction sequence, identify **P**, **Q**, **R** and **S** 

$$NH_{4}BF_{4} \xrightarrow[ethers]{NaBH_{4}in} P \xrightarrow[Al_{2}Cl_{6}]{} Q$$

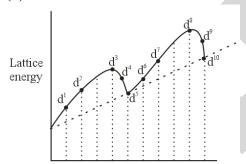
$$NaBH_{4}in \xrightarrow[ethers]{H_{2}O} R \xrightarrow{H_{2}O} S$$
(a) P = BF<sub>3</sub>, Q = BCl<sub>3</sub>, R = B<sub>2</sub>H<sub>6</sub>, S = B(OH)<sub>3</sub>
(b) P = NH<sub>4</sub>BO<sub>2</sub>, Q = B<sub>2</sub>Cl<sub>4</sub>, R = B(OH)<sub>3</sub>, S = B(OH)<sub>4</sub>
(c) P = NH<sub>4</sub>BO<sub>2</sub>, Q = B(OH)<sub>3</sub>, R = NaBO<sub>2</sub>, S = B(OH)<sub>3</sub>
(d) P = BF<sub>3</sub>, Q = B<sub>2</sub>Cl<sub>4</sub>, R = B(OH)<sub>3</sub>, S = B(OH)<sub>4</sub>
Ans. (a)
Sol. NH<sub>4</sub>BF<sub>4</sub>  $\xrightarrow[ether]{A}B_{2}H_{6}(R)$ 
BF<sub>3</sub>  $\xrightarrow[ether]{NaBH_{4}} B_{2}H_{6}(R)$ 
BF<sub>3</sub>  $\xrightarrow[ether]{Al_{2}Cl_{6}} BCl_{3}(Q)$ 

40. The correct order of CFSE for the ions in the complexes having same ligands is :

(a)  $V^{2+} < Mn^{2+} < Fe^{+2} < Co^{+2} < Ni^{+2}$ (b)  $V^{2+} > Mn^{2+} = Fe^{+2} > Co^{+2} = Ni^{+2}$ (c)  $Ni^{2+} < Co^{2+} < Fe^{+2} < Mn^{+2} < V^{+2}$ 

(d)  $Mn^{2+} < V^{2+} < Co^{+2} < Fe^{+2} < Ni^{+2}$ 

Ans. (d)



### Sol.

 $d^5$  and  $d^{10}$  show zero CFSE. The heights of other points above this reference dotted line is CFSE. (**Ref. J.D. Lee**)

- **41.** Complexes with.....geometry can exhibit different types of hybridization of central metal.
  - (a) square planar
  - (b) tetrahedral
  - (c) octahedral
  - (d) trigonal bipyramidal
- Ans. (b)
- **Sol.** Tetrahedral geometry can have two hybridization d<sup>3</sup>s and sp<sup>3</sup>
- 42. In the following given pairs, the one with an acidic oxide and a neutral oxide respectively is :-(a) NO, N<sub>2</sub>O (b) N<sub>2</sub>O<sub>5</sub>, NO (c) N<sub>2</sub>O, N<sub>2</sub>O<sub>5</sub> (d) N<sub>2</sub>O, NO

Ans. (b)

Sol.  $N_2O_5 \rightarrow \text{Acidic oxide}$ NO,  $N_2O \rightarrow \text{Neutral oxide}$  **43.** Out of the following substances, the one that forms a white, solid, has a high melting point and dissociates in water to form a basic solution is :-

(a) 
$$CO_2$$
 (b)  $P_4O_{10}$  (c)  $Na_2O$  (d)  $Cl_2O_7$ 

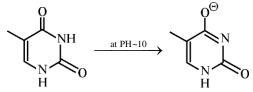
Ans. (c)

- **Sol.** Na<sub>2</sub>O is a basic oxide, which has a high melting point and is white solid, which dissociates and gives NaOH [base] on hydrolysis.
- 44. The form in which thymine, the base present in DNA, remains at  $pH \sim 10$ , is :-



Ans. (d)

Sol. At PH ~ 10, Thymine is deprotonated.



However none of the options contains anion.

 $\therefore$  the structure of anion most closely resembles (d).

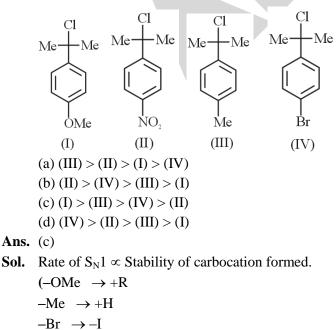
- 45. The compound not having a planar molecular configuration is :
  - (a)  $H_2C = CH_2$ (c)  $H_2C = C = CHCl$
- Ans. (c)
- **Sol.**  $\underset{H}{\overset{H}{\sim}} C = C = C \underset{Cl}{\overset{H}{\sim}} C$

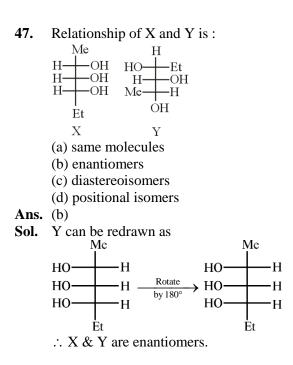
 $-NO_2 \rightarrow -R)$ 

46. For the following molecules, the correct order of reactivity towards  $S_N^{-1}$  reaction is :

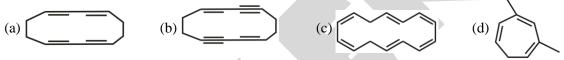
(b)  $H_2C = CH - C \equiv CH$ 

(d)  $H_2C = C = C = CH_2$ 





48. An unsaturated hydrocarbon "M" on oxidative ozonolysis gave a mixture of butanedioic acid and oxalic acid. The structure of the hydrocarbon "M" is :



Ans. (a,b)

- Both (a) & (b) give 2 eq. oxalic acid and 2 eq. Butane dioic acid each. Sol. : Both are correct
- An aqueous solution of  $CuSO_4(X)$  is treated with certain reagents. Identify the **incorrect** statement/s. **49**. (a) Addition of NH<sub>4</sub>OH to the aqueous solution of X develops green colour.

(b) X is treated with  $H_2S$  in acidic medium giving black precipitate soluble in hot aqueous KOH solution.

(c) X on treatment with KI in weakly acidic medium gives white precipitate of  $CuI_2$  liberating  $I_2$  gas.

(d) An aqueous solution of X when treated with  $BaCl_2$  solution gives white precipitate.

- Ans. (a,b,c)
- **Sol.** On addition of NH<sub>4</sub>OH, it will give Cu(OH)<sub>2</sub> blue ppt. On addition of H<sub>2</sub>S, X will give CuS black ppt. which is insoluble in KOH. On treatment with KI, X will give  $Cu_2I_2$  as white ppt. On treatment with  $BaCl_2$ , white ppt. of  $BaSO_4$  is produced.
- 50. Chlorine (Cl<sub>2</sub>) gas can be prepared by the action of concentrated (or Conc.)  $H_2SO_4$  on a mixture of sodium chloride (NaCl) and manganese dioxide ( $MnO_2$ ). Identify the set(s) of correct reactions.

(a) 
$$MnO_2 + H_2SO_4 \rightarrow MnSO_4 + H_2O + 1/2 O_2$$
  
 $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + Cl_2 + H_2$ 

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + Cl_2 + H_2SO_4 + H_2SO_4 + Cl_2 + H_2SO_4 + Cl_2 + H_2SO_4 + Cl_2 + H_2SO_4 +$$

(b)  $2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$ 

- $MnO_2 + 2HCl + H_2SO_4 \rightarrow MnSO_4 + Cl_2 + H_2O$
- (c)  $4NaCl + 4H_2SO_4 \rightarrow 4NaHSO_4 + 4HCl$
- $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$
- (d)  $MnO_2 + 2NaCl \rightarrow MnCl_2 + Na_2O + 1/2 O_2$

$$MnCl_2 + H_2SO_4 \rightarrow MnSO_4 + Cl_2 + H_2$$

Ans. (b,c)

**Sol.** NaCl with  $H_2SO_4$  prduces HCl, which is oxidized to  $Cl_2$  with MnO<sub>2</sub>.

- 51. The 18-valence electron rule asserts that transition metal compounds are thermodynamically stable when they have a total of 18 valence electrons on the central metal, which include the metal's d electrons and the electrons provided by the ligands attached to the metal. The 18-electron rule is obeyed by :

  (a) [Fe(CO)<sub>5</sub>]
  (b) [Mn(CO)<sub>5</sub>]
  (c) [Ni(CO)<sub>4</sub>]
  (d) [Cr(CO)<sub>6</sub>]
- Ans. (a,c,d)
- **Sol.** Compounds with EAN = 36, will have a total of 18 valence electrons on central metal.
- **52.** Identify the correct statement(s) from the following :
  - (a) The number bridging carbonyl groups in  $Co_2(CO)_8$  is 2
  - (b) The number of lone pair (s) in  $XeOF_4$  is zero
  - (c)  $B_5H_{10}$  is not an example of borane
  - (d) The number of bonding and lone pairs of electrons in  $XeF_2$  are 2 and 6, respectively.

Ans. (a,c)

(C) In general, borane polymers exists in general formula of  $B_nH_{n+4}$  [nido borane] and  $B_nH_{n+6}$  [arachano boranes]

**53.** Consider the following reaction :

$$\begin{array}{c} \begin{array}{c} \text{OCH}_2\text{CH}_3 \\ \text{H-C-OCH}_2\text{CH}_3 \\ \text{OCH}_2\text{CH}_3 \end{array} + \text{H}_2\text{C}=\text{CH-CHO} \xrightarrow{\text{NH}_4\text{NO}_3} \text{H}_2\text{C}=\text{CH-CH} \xrightarrow{\text{OCH}_2\text{CH}_3} + \begin{array}{c} \text{O} \\ \text{H-C-OCH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{O} \\ \text{H-C-OCH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{O} \\ \text{H-C-OCH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{H-C-CH-CHO} \\ \text{OCH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{H-C-CH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{O} \\ \text{H-C-OCH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{H-C-CH}_2\text{CH}_3 \end{array} + \begin{array}{c} \text{H-C-C-H}_2\text{CH}_3 \\ +$$

ethyl formate

triethyl orthoformate acrylaldehyde

The correct statement(s) pertinent to the above mentioned reaction is/are :

- (a) It is an example of acetal exchange reaction
- (b) It is an example of rearrangement reaction
- (c) Conventional reaction of acraldehyde and ethanol will produce better yield of the acetal
- (d) Water produced in the reaction is taken out of the equilibrium by the hydrolysis of the orthoester. (a d)
- Ans. (a,d)
- Sol. It is an acetal exchange reaction, with the orthoester being converted to ester and aldehyde to acetal. Conventional reaction of acrolein and ethanol can lead to nucleophilic addition on acrolein

(:: ethanol can act as nucleophile)

Water produced is used up in hydrolysis of orthoester to ester.

**54.** A 2 g piece of "dry ice" is dropped in a 5 L glass vessel containing air at 1 atm and 25°C and the vessel is sealed. After some time, dry ice disappeared

(Assume that the temperature is kept constant throughout)

Identify the **correct** statement(s).

- (a) Partial pressure of oxygen increases with respect to its initial value in air
- (b) Partial pressure of  $CO_2$  increases with respect to its initial value in air.
- (c) Total pressure of the vessel increases with respect to its initial value in air.
- (d) Disappearance of dry ice is due to the evaporation processs.

**Ans.** (b,c)

- **Sol.** (a)  $P_{O_{\gamma}}$  remain unchanged.
  - (b)  $P_{CO_{\gamma}}$  increases as its mole in gas is increasing.
  - (c) P<sub>total</sub> increases as the total moles of gases increases.
  - (d) Process is called sublimation.

**55.** A thermo-dynamical process is represented by the cycle shown below in which 0.1 mol of a perfect gas undergoes the reversible cyclic process  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$ 

$$\begin{array}{c} P/atm \\ 3.00 \\ B \\ 1.00 \\ A \\ \hline \\ 1000 \\ 2000 \\ V/cm^3 \end{array}$$

Given that  $C_{v,m} = \frac{3}{2}R$  independent of temperature.

All symbols have their usual meaning Identify the correct statement(s).

(a) 
$$T_B = 365.8 \text{ K}$$
  
(b)  $q_{B \to C} = 760.5 \text{ J}$   
(c)  $w_{B \to C} = -30 \text{ J}$   
(d)  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  for a perfect gas

Ans. (a,b,d)

Sol. (a) 
$$T_B = \frac{PV}{nR} = \frac{3 \times 1}{0.1 \times 0.082} = 365.8 \text{ K}$$
  
(b)  $q_{B\to C} = n.C_{P,m} \cdot (T_C - T_B) = 0.1 \times \frac{5}{2} \text{ R} \times (2T_B - T_B) = 760.43 \text{ J}$ 

- (c)  $w_{B\rightarrow C} = -P(V_C V_B) = -3(2 1) = -3$  atm-L =  $-3 \times 101.3 = -303.9$  J
- (d)  $\left(\frac{\partial U}{\partial V}\right)_{T} = 0$ , as the internal energy of fixed amount of an ideal gas is only the function of

temperature.

**56.** Identify the correct statement(s) for the binary solutions

(a) The volume of a solution at T and P equals the sum of the volumes of its pure components at T and P.

- (b) At constant T and P, the values of  $\Delta G_{mix}$  and  $\Delta S_{mix}$  are negative and positive respectively.
- (c) Inter-molecular interactions are negligible in an ideal solution.
- (d) The mixture of n-hexane and n-heptane form a nearly ideal solution.

Ans. (b,d)

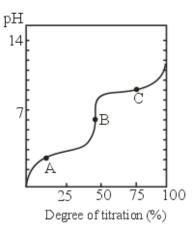
- **Sol.** (a)  $\Delta V_{mix} = 0$  only for ideal solution.
  - (b) For ideal as well as non-ideal solutions :  $\Delta G_{mix} = -ve$ ,  $\Delta S_{min} = +ve$ .
  - (c) Intermolecular interaction is not negligible.
  - (d) Informative.
- **57.** The heat of combustion (kJ mol<sup>-1</sup>) of ethane, propane and butane are -1560, -2220, -2878 respectively. When 100 g of each undergo complete combustion. Which of the following statement/s is/are correct?
  - (a) The heat generated by combustion of propane will be maximum
  - (b) The heat generated by combustion of butane will be maximum.
  - (c) At constant temperature and pressure, the work done during the combustion of ethane is minimum.

(d) At constant temperature and pressure, the work done during the combustion of butane is maximum.

**Ans.** (b,c,d)

$$\begin{aligned} & \text{Sol.} \quad q_{\text{ethane}} = -\frac{1560}{30} \times 100 = -5200 \text{ KJ} \\ & q_{\text{propane}} = -\frac{2220}{44} \times 100 = -5045.45 \text{ KJ} \\ & q_{\text{butane}} = -\frac{2878}{58} \times 100 = -4962.07 \text{ KJ} \\ & \text{w} = -\Delta n_{g}.\text{RT} \\ & C_{2}H_{6}(g) + \frac{7}{2} \text{ O}_{2}(g) \rightarrow 2\text{CO}_{2}(g) + 3\text{H}_{2}\text{O}(\ell); \Delta n_{g} = 2 - \left(1 + \frac{7}{2}\right) = -\frac{5}{2} \\ & C_{3}\text{H}_{8}(g) + 5\text{O}_{2}(g) \rightarrow 3\text{CO}_{2}(g) + 4\text{H}_{2}\text{O}(\ell); \Delta n_{g} = 3 - (1 + 5) = -3 \\ & C_{4}\text{H}_{10}(g) + \frac{13}{2} \text{ O}_{2}(g) \rightarrow 4\text{CO}_{2}(g) + 5\text{H}_{2}\text{O}(\ell); \Delta n_{g} = 4 - \left(1 + \frac{13}{2}\right) = -\frac{7}{2} \\ & (-\Delta n_{g}) : C_{2}\text{H}_{6} < \text{C}_{3}\text{H}_{8} < \text{C}_{4}\text{H}_{10} \end{aligned}$$

**58.** pH titration curve of aqueous solution of simple aliphatic amino acid with general formula  $NH_2$ -CHR-COOH (where R = Alkyl group) against NaOH is represented below.



Identify the **correct** statement(s) pertaining to it :

- (a) In aqueous solution, amino acid mainly exists as <sup>+</sup>NH<sub>3</sub>-CHR-COOH
- (b) At point 'A',  $[^{+}NH_{3}$ -CHR-COOH] =  $[^{+}NH_{3}$ -CHR-COO<sup>-</sup>]
- (c) At point 'B' amino acid exists in zwitter ion form.
- (d) At point 'C',  $[NH_2$ -CHR-COO<sup>-</sup>] = [<sup>+</sup>NH<sub>3</sub>-CHR-COO<sup>-</sup>]

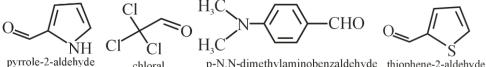
Ans. (a,b,c,d)

Sol.  $\overset{+}{NH}_3 - CHR - COOH \Longrightarrow \overset{+}{NH}_3 - CHR - COO^- \Longrightarrow NH_2 - CHR - COO^-$ 

- (a) Initial pH  $\rightarrow$  0. As the solution is highly acidic, amino acid will exist as  ${}^{+}_{NH_3}$  CHR COOH.
- (b) Buffer solution of  $\overset{+}{N}H_3 CHR COOH$  and  $\overset{+}{N}H_3 CHR COO^-$  with maximum buffer capacity.
- (c) First equivalent point.

Buffer solution of  $\overset{+}{NH}_3 - CHR - COO^-$  and  $NH_2 - CHR - COO^-$  with maximum buffer capacity.

Tendency to undergo Cannizaro reaction depends upon the electrophilic nature of the carbonyl group. 59.



p-N,N-dimethylaminobenzaldehyde thiophene-2-aldehyde chloral

Identify the incorrect statement(s) from those listed below

(a) Thiophene-2-aldehyde will undergo Cannizaro reaction

(b) Only chloral will not undergo Cannizaro reaction but others will follow.

(c) pyrrole-2-aldehyde, chloral and p-N,N-dimethylaminobenzaldehyde will not follow Cannizaro reaction

(d) All the four molecules will undergoes Cannizaro reaction since no one contains any enolisable  $\alpha$ hydrogen atom.

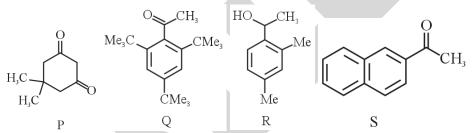
- **Ans.** (b,d)
- Sol. Thiophene-2-aldehyde undergoes cannizzaro reaction.

Pyrrole-2-aldehyde will not undergo since it does acid-base reaction with OH<sup>-</sup>.

Chloral undergoes SNAE (similar to haloform reaction)

p-N, N-dimethyl aminobenzene has high electron density, so less electrophilic carbonyl.

In the haloform reaction, the trihalogenated intermediate  $(-CO-CX_3)$  formed is then subjected to a 60. nucleophilic attack by the hydroxide ion (OH<sup>-</sup>) at the carbon (C=O) producing a tetrahedral intermediate, which eventually breaks down, expelling the -CX3 group and leading to the formation of a carboxylate anion.



Identify the **correct** statement(s) regarding iodoform reaction.

- (a) 'Q', 'R' and 'S' will take part in iodoform reaction
- (b) 'P', 'R' and 'S' will take part in iodoform reaction
- (c) 'P' and 'Q' will not take part in iodoform reaction
- (d) 'Q' will not take part in iodoform reaction

**Ans.** (b,d)

Only Q does not give iodoform reaction due to steric hindrance at carbonyl. Rest all 3 give iodoform Sol. reaction (P through active methylene group, while, R is first oxidised to methyl ketone)