

- Sol. Both Statement-I and Statement-II are correct.

$$\begin{array}{c} CH_{3} \\ CH_{3}-C-CH_{3}+X_{2} \xrightarrow{hv} CH_{3}-C-CH_{2}-X \\ CH_{3} \\ (X=Cl, Br) \end{array}$$
melting point $\swarrow > \checkmark$

neo-pentane n-pentane

54. Which among the following molecules is (a) involved in sp³d hybridization, (b) has different bond lengths and (c) has lone pair of electrons on the central atom ?

(1)
$$PF_5$$
 (2) XeF_4
(3) SF_4 (4) XeF_2

Ans. (3)

 XeF_4 :- sp^3d^2 Hybridisation

SF₄:-
$$F$$
 (a) Hybridisation = sp³d
(b) All bonds are not identical
F (c) 1 lone pair on central atom

XeF₂:- (a) Hybridisation = sp³d F-Xe-F (b) All bonds are identical (c) 3 lone pair on central atom

55. Formation of Na₄[Fe(CN)₅NOS], a purple coloured complex formed by addition of sodium nitroprusside in sodium carbonate extract of salt indicates the presence of :

(1) Sodium ion	(2) Sulphate ion
(3) Sulphide ion	(4) Sulphite ion

- Ans. (3)
- Sol. $Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$ Sodium sulphide Sodium nitro Prusside Prosside

Ans. (1)



4-sp³, 2-sp², 2-sp

57. Which of the following statements are **true** ?

(A) The subsidiary quantum number *l* describes the shape of the orbital occupied by the electron.



diagram of the 2px orbital.

(C) The + and - signs in the wave function of the $2p_x$ orbital refer to charge.

(D) The wave function of $2p_x$ orbital is zero everywhere in the xy plane.

- (1) (B) and (D) only
- (2) (A), (B) and (C) only
- (3) (C) and (D) only
- (4) (A) and (B) only

Ans. (4)

Sol. (A) Azimuthal quantum number (ℓ) indicates the shape of orbital occupied by the electron

(B)
$$x p_x$$
 orbital

- (C) The + and sign in the wave function of $2p_x$ orbital refer to the sign (Phase) of the wave function , not the charge
- (D) The wave function of $2p_x$ orbital will be zero in yz plane (Nodal plane).

- **58.** The type of hybridization and the magnetic property of $[MnCl_6]^{3-}$ are :
 - (1) d^2sp^3 , paramagnetic with four unpaired electrons
 - (2) sp^3d^2 , paramagnetic with four unpaired electrons
 - (3) d^2sp^3 , paramagnetic with two unpaired electrons
 - (4) sp^3d^2 , paramagnetic with two unpaired electrons

Ans. (2)

Sol. $[MnCl_6]^{3-}$ contains Mn^{+3} $Mn^{+3} :- [Ar]3d^4$ Ligand $\Rightarrow Cl^- (WFL)$ $3d^4$ 1 1

> Hybridisation = sp^3d^2 4 unpaired electrons

59. Consider the following reactions. From these reactions which reaction will give carboxylic acid as a major product ?

(A)
$$R - C \equiv N \xrightarrow{(i)H^+/H_2O}{\text{mild condition}}$$

(B) $R - MgX \xrightarrow{(i)CO_2}{(ii)H_3O^+}$
(C) $R - C \equiv N \xrightarrow{(i)SnCl_2/HCl}{(ii)H_3O^+}$
(D) $R \cdot CH_2 \cdot OH \xrightarrow{PCC}$

(E)
$$\leftarrow$$
 COCl $\xrightarrow{(i)H_2|Pd-BaSO_4}$ (ii)Br₂ water

Choose the **correct** answer from the options given below :

- (1) A and D only
- (2) A, B and E only
- (3) B, C and E only
- (4) B and E only

Ans. (4)

Sol. (A) $R - C \equiv N \xrightarrow{(i)H^+/H_2O} R - CONH_2$

Under mild condition amide is formed because this reaction is typically slow if further more heat will supplied then it gets convert in to –COOH.

(B)
$$R - MgX \xrightarrow{(i)CO_2} R - COOH$$

(C)
$$R - C \equiv N \xrightarrow{(1)SnCl_2/HCl} R - CHO$$

(ii) $H_3O^+ \rightarrow R - CHO$

(D)
$$R \cdot CH_2 \cdot OH \xrightarrow{PCC} R - CHO$$

(E)
$$-COCl \xrightarrow{H_2/Pd-BaSO_4}$$
 $-CHO$
 Br_2/H_2O
(Mild oxidizing agent)

60. Electronic configuration of four elements A, B, C and D are given below :

(A)
$$1s^22s^22p^3$$
 (B) $1s^22s^22p^4$
(C) $1s^22s^22p^5$ (D) $1s^22s^22p^2$

Which of the following is the correct order of increasing electronegativity (Pauling's scale) ?

(1)
$$A < D < B < C$$

(2) $A < C < B < D$
(3) $A < B < C < D$
(4) $D < A < B < C$

Ans. (4)

Sol. N :- $1s^2 2s^2 2p^3$ (Electronegativity = 3) O :- $1s^2 2s^2 2p^4$ (Electronegativity = 3.5) F :- $1s^2 2s^2 2p^5$ (Electronegativity = 4) C :- $1s^2 2s^2 2p^2$ (Electronegativity = 2.55) Correct order = C > B > A > D

61. Match List-I with List-II

List-I		List-II		
(Purification		(Mixture of organic		
	technique)	compounds)		
(A)	Distillation	(I)	Diesel + Petrol	
	(simple)			
(B)	Fractional	(II)	Aniline + Water	
	distillation			
(C)	Distillation	(III)	Chloroform +	
	under reduced		Aniline	
	pressure			
(D)	Steam	(IV)	Glycerol +	
	distillation		Spent-lye	

Choose the **correct** answer from the options given below :

(1) (A)-(II), (B)-(III), (C)-(IV), (D)-(I)

(2) (A)-(II), (B)-(IV), (C)-(I), (D)-(III)

(3) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

(4) (A)-(III), (B)-(I), (C)-(IV), (D)-(II)

Ans. (4)



(Pu	List-I rification technique)	List-II (Mixture of organic compounds)	
(A)	Distillation (simple)	(III)	Chloroform + Aniline
(B)	Fractional distillation	(I)	Diesel + Petrol
(C)	Distillation under reduced pressure	(IV)	Glycerol + Spent-lye
(D)	Steam distillation	(II)	Aniline + Water

62. 'x' g of NaCl is added to water in a beaker with a lid. The temperature of the system is raised from 1°C to 25°C. Which out of the following plots, is best suited for the change in the molarity (M) of the solution with respect to temperature ?
[Consider the solubility of NaCl remains unchanged over the temperature range]



- **63.** Arrange the following in order of magnitude of work done by the system / on the system at constant temperature :
 - (a) $|w_{\text{reversible}}|$ for expansion in infinite stage.
 - (b) $|w_{irreversible}|$ for expansion in single stage.
 - (c) $|w_{reversible}|$ for compression in infinite stage.
 - (d) $|w_{irreversible}|$ for compression in single stage.

Choose the **correct** answer from the options given below :

(1)
$$a > b > c > d$$

(2)
$$d > c = a > b$$

(3) c = a > d > b

(4)
$$a > c > b > d$$

Ans. (2)

Sol. For isothermal process

 $|W_{reversible}|_{expansion} = |W_{reversible}|_{compression}$

$$=$$
 - nRT ln $\frac{V_{f}}{V_{i}}$

 $|W_{irreversible}|_{expansion} < |W_{irreversible}|_{compression}$ d > c = a > b

 $|W_{irreversible}|_{expansion} = -P_{ext} (V_f - V_i)$



Which of the following represents the above reaction mechanism?



65. The nature of oxide (TeO₂) and hydride (TeH₂) formed by Te, respectively are :

- (1) Oxidising and acidic
- (2) Reducing and basic
- (3) Reducing and acidic
- (4) Oxidising and basic
- Ans. (1)
- Sol. TeO_2 is oxidizing in nature because it can be reduced from +4 oxidation state to lower oxidation state.

 TeH_2 due to less bond dissociation energy easily breaks and hence acidic in nature.

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66. Match List-I with List-II

List-I		List-II		
(Reaction)		(Name of		
	reaction)			
2 X+2Na $\xrightarrow{\text{Dry}}$	(I)	Lucas		
+2Na		reaction		
$ArN_{2}^{+}X^{-} \xrightarrow{Cu}_{HCl} \rightarrow ArCl + N_{2} \uparrow + CuX$	(II)	Finkelstein		
		reaction		
$C_2H_5Br + NaI \xrightarrow{Dry} C_2H_5I + NaBr$	(III)	Fittig		
		reaction		
$CH_{3}C(OH)(CH_{3})CH_{3} \xrightarrow{HCl}{ZnCl_{2}}$	(IV)	Gatterman		
CH ₃ C(Cl)(CH ₃)CH ₃		reaction		
	List-I (Reaction) $2 \underbrace{ -X + 2Na \xrightarrow{Dy} \underbrace{ -X + 2Na}_{Bhr} \underbrace{ -X + 2Na}_{+2Na} \underbrace{ -X + 2Na}_{+2Na} \underbrace{ -X + 2Na}_{+2Na} \underbrace{ -X + 2Na}_{-X + 2Na} -X$	$\begin{array}{c} \text{List-I} & (Reaction) &$		

Choose the correct answer from the options given below :

(1) (A)-(III), (B)-(II), (C)-(IV), (D)-(I)

(2) (A)-(III), (B)-(IV), (C)-(II), (D)-(I)

(3) (A)-(IV), (B)-(III), (C)-(I), (D)-(II)

(4) (A)-(IV), (B)-(I), (C)-(II), (D)-(III)



Sol.				
	List-I		List-II	
	(Reaction)		(Name of	
		r	eaction)	
(A)	$2 \left(\bigcirc X + 2 \text{Na} \xrightarrow{\text{Dry}} \left(\bigcirc Y \right) \right)$	(III)	Fittig reaction	
(B)	$ArN_{2}^{+}X^{-} \xrightarrow{Cu}_{HCl} \rightarrow ArCl + N_{2} \uparrow + CuX$	(IV)	Gatterman reaction	
(C)	$C_2H_5Br + NaI \xrightarrow{Dry}{Acetone} C_2H_5I + NaBr$	(II)	Finkelstein reaction	
(D)	$CH_{3}C(OH)(CH_{3})CH_{3} \xrightarrow{HCl}_{ZnCl_{2}} \rightarrow CH_{3}C(Cl)(CH_{3})CH_{3}$	(I)	Lucas reaction	

67. Consider the following chemical equilibrium of the gas phase reaction at a constant temperature : $A(g) \rightleftharpoons B(g) + C(g)$

If p being the total pressure, K_p is the pressure equilibrium constant and α is the degree of dissociation, then which of the following is true at equilibrium ?

- (1) If p value is extremely high compared to $K_p, \alpha \approx 1$
- (2) When p increases α decreases
- (3) If k_p value is extremely high compared to p, α becomes much less than unity
- (4) When p increases α increases

Ans. (2)

Sol.

$$A(g) \Longrightarrow B(g) + C(g)$$

 $t = 0 \quad a \quad 0 \quad 0 \\ t = t \quad a (1 - \alpha) \quad a \alpha \quad a \alpha$

a moles of A(g) taken initially and at time Now moles fraction of A(g), B(g) and C(g) are

$$X_{A} = \frac{a - a\alpha}{a + a\alpha} = \frac{1 - \alpha}{1 + \alpha}$$
$$X_{B} = \frac{a\alpha}{a + a\alpha} = \frac{\alpha}{1 + \alpha}$$
$$X_{C} = \frac{a\alpha}{a + a\alpha} = \frac{\alpha}{1 + \alpha}$$

Now if P is total pressure then partial pressure of A(g), B(g) and C(g) are

$$P_{A} = \left(\frac{1-\alpha}{1+\alpha}\right)P$$

$$P_{B} = \left(\frac{\alpha}{1+\alpha}\right)P$$

$$P_{C} = \left(\frac{\alpha}{1+\alpha}\right)P$$

$$K_{P} = \frac{\left(\frac{\alpha}{1+\alpha}\right)P\left(\frac{\alpha}{1+\alpha}\right)P}{\left(\frac{1-\alpha}{1+\alpha}\right)P}$$

$$K_{P} = \frac{\alpha^{2} P}{1-\alpha^{2}}$$

As K_P is only function of temperature. So as $P \uparrow \alpha \downarrow$

68. Which of the following graphs correctly represents the variation of thermodynamic properties of Haber's process ?

$$(1) \begin{array}{c} 300 \\ 200 \\ 100 \\ -\Delta G_{R}^{\theta} / T \\ 0 \\ -100 \\ -200 \\ -200 \\ -\Delta S_{R}^{\theta} \\ -200 \\ -\Delta H_{R}^{\theta} \\ -200 \\ -\Delta H_{R}^{\theta} \\ 100 \\ -\Delta G_{R}^{\theta} / T \end{array}$$

$$(2) \xrightarrow{-\Delta G_{R}^{\theta} / T} \xrightarrow{-100} \xrightarrow{\Delta H_{R}^{\theta} / T} \xrightarrow{T/K} \xrightarrow{-200} \xrightarrow{\Delta S_{R}^{\theta} / T}$$

$$\begin{array}{c|c}
200 & \Delta S_{R}^{\theta} \\
100 & \Delta H_{R}^{\theta} \\
0 & & \\
(3) & -100 & & \\
-200 & & -\Delta H_{R}^{\theta} / T \\
\end{array}$$

$$(4) \begin{array}{c} 300 \\ 200 \\ 100 \\ -\Delta H_{R}^{\theta} / T \\ -100 \\ -200 \\ \Delta S_{R}^{\theta} \end{array} T/K \rightarrow$$

Ans. (1)

Sol. $N_2(g) + 3H_2(g) \rightarrow 2NH_3$

 $\Delta H^{\circ} = -ve$

 $\Delta S^{\circ} = -ve$

(As gaseous moles decreases).

- (1) As temperature increases $\frac{-\Delta H_R^o}{T}$, decreases
- (2) $\Delta G^{\circ} = -RT \ln K_{eq}$
- $R \ln K_{eq} = -\frac{\Delta G^o}{T}$

(on increasing temperature in exothermic reaction K_{eq} decreases)

 ΔH° and ΔS° are almost constant with temperature.

- **69.** A tetrapeptide "*x*" on complete hydrolysis produced glycine (Gly), alanine (Ala), valine (Val), leucine (Leu) in equimolar proportion each. The number of tetrapeptides (sequences) possible involving each of these amino acids is
 - (1) 16 (2) 32
 - (3) 8 (4) 24
- Ans. (24)
- **Sol.** The number of tetrapeptides (sequences) possible involving each of these amino acids (glycine, alanine, valine, leucine); It has three (3) peptides linkage the number of permutations in which they can be arranged
 - $= 4 \times 3 \times 2 \times 1$
 - = 24
- 70. In Dumas' method for estimation of nitrogen, 0.5 gram of an organic compound gave 60 mL of nitrogen collected at 300 K temperature and 715 mm Hg pressure. The percentage composition of nitrogen in the compound (Aqueous tension at 300 K = 15 mm Hg) is
 - (1) 1.257 (2) 20.87
 - (3) 18.67 (4) 12.57
- Ans. (4)
- **Sol.** Pressure of N_2 gas = (715 15)
 - = 700 mmHg

$$n_{N_2} = \frac{P}{R}$$

$$n_{N_2} = \frac{700 \times 60 \times 10^{-3}}{760 \times 0.0821 \times 300}$$

$$= 2.24 \times 10^{-3} \text{ mol}$$

Mass of
$$N_2 = 2.24 \times 10^{-3} \times 28g$$

$$%N_2 = \frac{0.06272}{0.5} \times 100 \approx 12.57$$

SECTION-B

71. For the reaction A → B the following graph was obtained. The time required (in seconds) for the concentration of A to reduce to 2.5 g L⁻¹ (if the initial concentration of A was 50 g L⁻¹) is _____. (Nearest integer)





Allen Ans. (BONUS)

NTA Ans. (43)

Sol. As it is difficult to predict order using data provided in graph.
For specific time interval 0 - 5 sec, 5 - 10 sec and

10 - 15 sec. order comes to be zero, but graph is not a straight line. Assuming 1^{st} order kinetics

Assuming 1th order kinetic

$$K = \frac{1}{t} \ln \frac{A_0}{A_t}$$
$$K = \frac{1}{10} \ln \frac{40}{20}$$

Time required to reduce to 2.5 g/L

$$K = \frac{1}{t} \ln \frac{50}{2.5}$$
$$\frac{1}{10} \ln 2 = \frac{1}{t} \ln 20$$
$$t = \frac{1.3010 \times 10}{0.3010} = 43.3 \text{ sec.}$$

72. 0.2 % (w/v) solution of NaOH is measured to have resistivity 870.0 m Ω m. The molar conductivity of the solution will be _____×10² mS dm² mol⁻¹. (Nearest integer)

Ans. (23)

Sol. Given : Concentration of NaOH = 0.2% (w/v)
∴ 0.2 g of NaOH in 100 ml of solution.
Molarity of NaOH solution

$$= \frac{\text{moles of solute}}{V_{\text{ml}}} \times 1000$$
$$= \frac{0.2/40}{100} \times 1000 = \frac{0.2}{40 \times 100} \times 1000 = \frac{2}{40} \text{ M}$$

Given resistivity of solution = 870 m ohm m

- $= 870 \times 10^{-3}$ ohm m
- $= 870 \times 10^{-3} \times 10$ ohm dm
- $= 870 \times 10^{-2}$ ohm dm
- = 8.7 ohm dm

Now conductivity

$$K = \frac{1}{\rho} = \frac{1}{8.7} \text{ ohm}^{-1} \text{ dm}^{-1}$$

Now molar conductivity of solution is

$$\lambda_{\rm m} = \frac{\rm K}{\rm M} = \frac{\frac{1}{8.7}}{\frac{2}{40}} = \frac{40}{2 \times 8.7} = 2.29 \,\,{\rm S}\,\,{\rm dm}^2\,{\rm mol}^{-1}$$

$$2.29 \times 10^3 \,{\rm m}\,{\rm S}\,\,{\rm dm}^2\,{\rm mol}^{-1}$$

$$= 22.9 \times 10^2 \,{\rm m}\,{\rm S}\,\,{\rm dm}^2\,{\rm mol}^{-1}$$

$$= 23 \times 10^2 \,{\rm m}\,{\rm S}\,\,{\rm dm}^2\,{\rm mol}^{-1}$$

Consider the above sequence of reactions. 151 g of 2-bromopentane is made to react. Yield of major product P is 80% whereas Q is 100%. Mass of product Q obtained is _____ g. (Given molar mass in g mol⁻¹ H: 1, C : 12, O : 16, Br : 80)

Br,

▶0

73.







Molecular mass of Q = $230 \text{g} \text{ mol}^{-1}$ Mass of Q = 0.8×230 = 184 g

74. When 1 g each of compounds AB and AB₂ are dissolved in 15 g of water separately, they increased the boiling point of water by 2.7 K and 1.5 K respectively. The atomic mass of A (in amu) is $___\times10^{-1}$ (Nearest integer)

(Given : Molal boiling point elevation constant is $0.5 \text{ K kg mol}^{-1}$)

Ans. (25)

Sol. For AB

 $\Delta T_b = 2.7 \text{ K}$ $2.7 = 1 \times 0.5 \times \text{m}$

$$m = \frac{27}{5}$$

Let molar mass of AB = x.

So
$$\frac{1/x}{15} \times 1000 = \frac{27}{5}$$

x = 12.34
For AB₂
 $\Delta T_b = 1.5 \text{ K}$
1.5 = 1 × 0.5 × m
m = 3
Let molar mass of AB₂ = y
So $\frac{1/y}{15} \times 1000 = 3$

 $y = \frac{1000}{45}$ y = 22.22

y = 22.22

Now let a and b be atomic masses of A and B respectively, then

75. The spin-only magnetic moment value of Mⁿ⁺⁻ ion formed among Ni, Zn Mn and Cu that has the least enthalpy of atomisation is _____. (in nearest integer)

Here n is equal to the number of diamagnetic complexes among K_2 [NiCl₄], [Zn (H₂O)₆] Cl₂,

K₃[Mn(CN)₆] and [Cu(PPh₃)₃I]

Ans. (0)

Sol. $K_2[NiCl_4] \Rightarrow sp^3$, Paramagnetic $[Zn(H_2O)_6]Cl_2 \Rightarrow sp^3d^2$, Diamagnetic $K_3[Mn(CN)_6] \Rightarrow d^2sp^3$, Paramagnetic $[Cu(PPh_3)_3I] \Rightarrow sp^3$, Diamagnetic Hence the value of n is 2 Least value of enthalpy of atomisation among Ni, Zn, Mn and Cu is of Zn Zn^{+2} :- $[Ar]3d^{10}$ $\mu = 0$