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Chemistry

PART – III
SECTION – I

Straight Objective Type

This section contains 6 multiple choice questions. Each question has 4 choices (A), (B), (C) and (D), out of which **ONLY ONE** is correct.

47. 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

Sol. **(B)**
Ag dissociates in a solution of NaCN in the presence of air, and forms sodium argentocyanide.

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na\left[Ag(CN)_2\right] + 4NaOH$$

48. 2.5 mL of $\frac{2}{5}$M weak monoacidic base $\left(K_b = 1\times10^{-12} \text{ at } 25^0C\right)$ is titrated with $\frac{2}{15}$M HCl in water at 25°C. The concentration of H^+ at equivalence point is $\left(K_w = 1\times10^{-14} \text{ at } 25^0C\right)$
(A) 3.7×10^{-13}M (B) 3.2×10^{-7}M
(C) 3.2×10^{-2}M (D) 2.7×10^{-2}M

Sol. **(D)**

$$BOH + HCl \longrightarrow \underset{C}{BCl} + H_2O$$

$$\underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{Ch}{BOH} + \underset{Ch}{H^+}$$

$$\text{Volume of HCl used} = \frac{2.5\times\frac{2}{5}}{2/15} = 7.5\,\text{ml}$$

$$\text{Concentration of Salt, C} = \frac{2.5\times\frac{2}{5}}{10} = 0.1\text{M}$$

$$\therefore \frac{Ch^2}{1-h} = \frac{K_w}{K_b}$$

Solving h = 0.27

$$\left[H^+\right] = Ch = 0.1\times0.27 = 2.7\times10^{-2}\text{ M}$$

49. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reactions is
(A) 0.5 mol^{-1} dm^3 (B) 1.0 mol dm^{-3}
(C) 1.5 mol dm^{-3} (D) 2.0 mol^{-1} dm^3

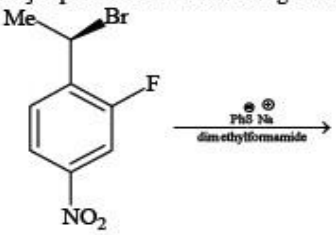
Sol. **(A)**

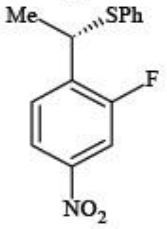
$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}$$

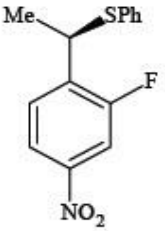
$$k_0 = \frac{A_0}{2t_{1/2}} = \frac{1.386}{2\times20}$$

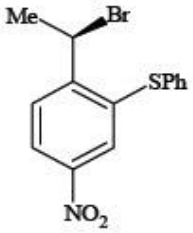
$$\frac{k_1}{k_0} = \frac{0.693}{40}\times\frac{40}{1.386} = \frac{0.693}{1.386} = 0.5\text{ mol}^{-1}\text{litre}$$

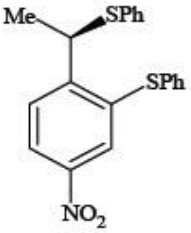
50. The major product of the following reaction is



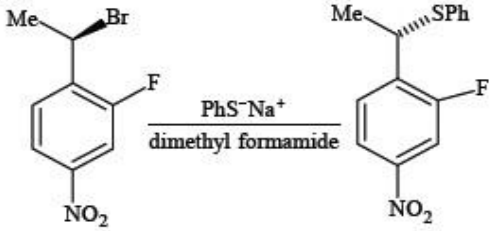
(A) 

(B) 

(C) 

(D) 

Sol. (A)



It is easier to do nucleophilic substitution on alkyl halides than on aryl halides.

51. Hyperconjugation involves overlap of the following orbitals

(A) σ - σ (B) σ - p

(C) p – p (D) π - π

Sol. **(B)**

Hyperconjugation involves overlap of σ – p orbitals.

52. Aqueous solutions of $Na_2S_2O_3$ on reaction with Cl_2 gives

(A) $Na_2S_4O_6$ (B) $NaHSO_4$

(C) NaCl (D) NaOH

Sol. **(B)**

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O \longrightarrow 2NaHSO_4 + 8HCl$$

SECTION – II

Multiple Correct Answers Type

This section contains 4 multiple correct answer(s) type questions. Each question has 4 choices (A), (B), (C) and (D), out of which **ONLY OR MORE** is/are correct.

53. A gas described by van der Waal's equation
(A) behaves similar to an ideal gas in the limit of large molar volumes
(B) behaves similar to an ideal gas in the limit of large pressures
(C) is characterized by van der Waal's coefficients that are dependent on the identify of the gas but are independent of the temperature
(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

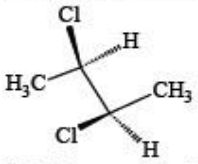
Sol. **(A, C, D)**

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb)=nRT$$

At low pressure, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly.

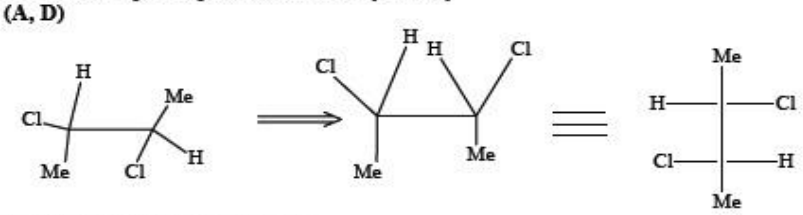
a and b are characteristic of a gas and are independent of temperature. The term $\left(P+\frac{n^2a}{V^2}\right)$ represents the pressure exerted by an ideal gas while P represents the pressure exerted by a real gas.

54. The correct statement (s) about the compound given below is (are)

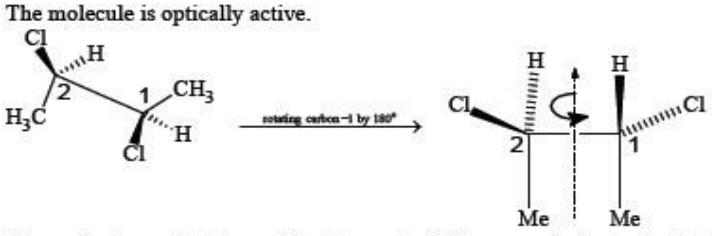


(A) The compound is optically active
(B) The compound possesses centre of symmetry
(C) The compound possesses plane of symmetry
(D) The compound possesses axis of symmetry

Sol. **(A, D)**

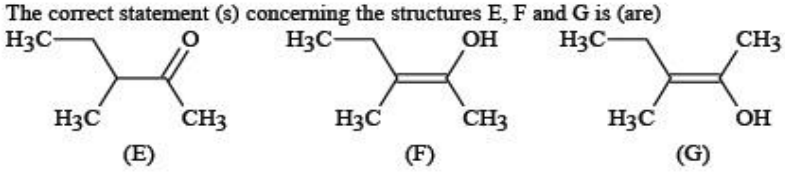


The molecule is optically active.



The molecule possesses an axis of symmetry (C_2) perpendicular to the C – C bond.

55. The correct statement (s) concerning the structures E, F and G is (are)



(A) E, F and G are resonance structures
(B) E, F and E, G are tautomers
(C) F and G are geometrical isomers
(D) F and G are diasteromers

Sol. **(B), (C), (D)**

56. A solution of colourless salt **H** on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt (s) **H** is (are)

(A) NH_4NO_3
(B) NH_4NO_2
(C) NH_4Cl
(D) $(NH_4)_2SO_4$

Sol. **(A, B)**

$$NH_4NO_3 + NaOH \longrightarrow NH_3 + NaNO_3 + H_2O$$

$$7NaOH + NaNO_3 + 4Zn \rightarrow 4Na_2ZnO_2 + NH_3 + 2H_2O$$

$$NH_4NO_2 + NaOH \rightarrow NaNO_2 + NH_3 + H_2O$$

$$3Zn + 5NaOH + NaNO_2 \rightarrow 3Na_2ZnO_2 + NH_3 + H_2O$$

SECTION – III
Reasoning Type

This section contains 4 reasoning type questions. Each question has 4 choices (A), (B), (C) and (D), out of which **ONLY ONE** is correct.

57. **STATEMENT-1:** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

and

STATEMENT-2: At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

(A) STATEMENT – 1 is True, STATEMENT-2 is True; STATEMENT -2 is correct explanation for STATEMENT-1
(B) STATEMENT – 1 is True, STATEMENT-2 is True; STATEMENT -2 is NOT a correct explanation for STATEMENT-1
(C) STATEMENT – 1 is True, STATEMENT-2 is False
(D) STATEMENT – 1 is False, STATEMENT-2 is True

Sol. **(D)**

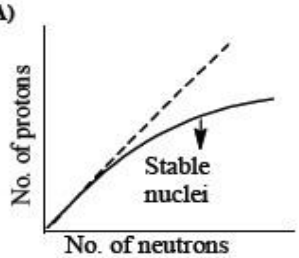
At equilibrium $\Delta G = 0$, ΔG° of a reaction may or may not be zero.

For a spontaneous process $\Delta G < 0$

58. **STATEMENT-1:** The plot of atomic number (y-axis) versus number of neutrons (x-axis) for stable nuclei shows a curvature towards x-axis from the line of 45° slope as the atomic number is increased.
and
STATEMENT-2: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons and neutrons in heavier nuclides.

(A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is correct explanation for STATEMENT-1
(B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
(C) STATEMENT-1 is True, STATEMENT-2 is False
(D) STATEMENT-1 is False, STATEMENT-2 is True

Sol. **(A)**



If the curve does not bend down towards the x axis then the proton-proton repulsion would overcome the attractive force of proton and neutron. Therefore, the curve bends down.

59. **STATEMENT-1:** Bromobenzene upon reaction with Br_2/Fe gives 1, 4 – dibromobenzene as the major product.

and

STATEMENT-2: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

(A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is correct explanation for STATEMENT-1
(B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
(C) STATEMENT-1 is True, STATEMENT-2 is False
(D) STATEMENT-1 is False, STATEMENT-2 is True

Sol. **(C)**
In bromobenzene, it is the mesomeric effect which directs the incoming electrophile.

60. **STATEMENT-1:** Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds.
and
STATEMENT-2: The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.

(A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is correct explanation for STATEMENT-1
(B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1
(C) STATEMENT-1 is True, STATEMENT-2 is False
(D) STATEMENT-1 is False, STATEMENT-2 is True

Sol. **(C)**
The lower oxidation states for the group 14 elements are more stable for the heavier member of the group due to inert pair effect.

SECTION – IV

Linked Comprehension Type

This section contains 3 paragraphs. Based upon each paragraph, 3 multiple choice questions have to be answered. Each question has 4 choices (A), (B), (C) and (D), out of which **ONLY ONE** is correct.

Paragraph for Question Nos. 61 to 63

There are some deposits of nitrates and phosphates in earth's crust. Nitrates are more soluble in water. Nitrates are difficult to reduce under the laboratory conditions but microbes do it easily. Ammonia forms large number of complexes with transition metal ions. Hybridization easily explains the ease of sigma donation capability of NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorus.

61. Among the following, the correct statement is

(A) Phosphates have no biological significance in humans
(B) Between nitrates and phosphates, phosphates are less abundant in earth's crust
(C) Between nitrates and phosphates, nitrates are less abundant in earth's crust
(D) Oxidation of nitrates is possible in soil

Sol. **(C)**

62. Among the following, the correct statement is

(A) Between NH_3 and PH_3, NH_3 is better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
(B) Between NH_3 and PH_3, PH_3 is better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(C) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional
(D) Between NH_3 and PH_3, PH_3 is better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional

Sol. **(C)**
On going from top to bottom in nitrogen group the bond angle decreases due to more p-character in the bond pair and subsequently more s-character in lone pair orbital.

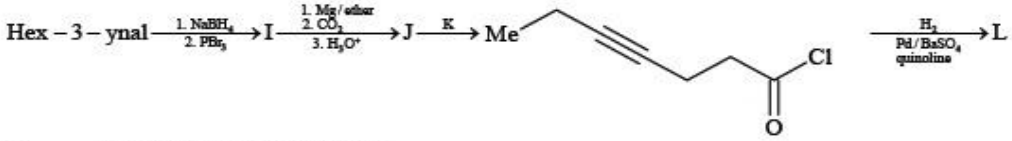
63. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
(A) dimerization reaction (B) disproportionation reaction
(C) condensation reaction (D) precipitation reaction

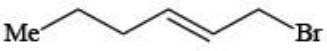
Sol. **(B)**

$$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$$

Paragraph for Question Nos. 64 to 66

In the following sequence, products I, J and L are formed. K represents a reagent.



64. The structure of the product I is
(A) 

(B) 

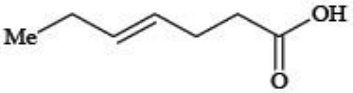
(C) 

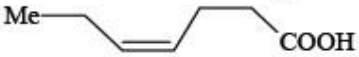
(D) 

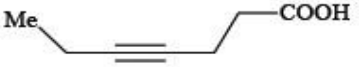
Sol. **(D)**

$$CH_3 - CH_2 - C \equiv C - CH_2 - CHO \xrightarrow[2.\ PBr_3]{1.\ NaBH_4} CH_3 - CH_2 - C \equiv C - CH_2 - CH_2Br$$

65. The structures of compounds J and K respectively are
(A) 

and $SOCl_2$
(B) 

and SO_2Cl_2
(C) 

and $SOCl_2$
(D) 

and CH_3SO_2Cl

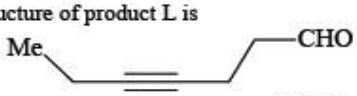
Sol. **(A)**

$$CH_3 - CH_2 - C \equiv C - CH_2 - CH_2Br \xrightarrow[3.\ H_3O^+]{1.\ Mg\ /\ Ether\ 2.\ CO_2} J \xrightarrow{K} CH_3 - CH_2 - C \equiv C - CH_2 - COCl$$

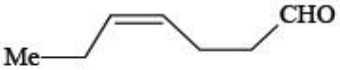
$J = CH_3 - CH_2 - C \equiv C - CH_2 - COOH$

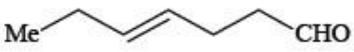
$K = SOCl_2$

Hence, (A) is the correct answer.

66. The structure of product L is
(A) 

(B) 

(C) 

(D) 

Sol. **(C)**

Paragraph for Question Nos. 67 to 69

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given: Freezing point depression constant of water $\left(K_f^{water}\right) = 1.86\ K\ kg\ mol^{-1}$

Freezing point depression constant of ethanol $\left(K_f^{ethanol}\right) = 2.0\ K\ kg\ mol^{-1}$

Boiling point elevation constant of water $\left(K_b^{water}\right) = 0.52\ K\ kg\ mol^{-1}$

Boiling point elevation constant of ethanol $\left(K_b^{ethanol}\right) = 1.2\ K\ kg\ mol^{-1}$

Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K
Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40 mm Hg
Molecular weight of water = 18 g mol^{-1}
Molecular weight of ethanol = 46 g mol^{-1}

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

67. The freezing point of the solution **M** is

(A) 268.7 K (B) 268.5 K
(C) 234.2 K (D) 150.9 K

Sol. **(D)**

$$\Delta T_f = K_f \times m$$

$$2 \times \frac{0.1}{0.9 \times 46} \times 1000 = 4.83\ K$$

Freezing point of solution M = 155.7 – 4.83 = 150.87 K $\approx$ 150.9 K

68. The vapour pressure of the solution **M** is

(A) 39.3 mm Hg (B) 36.0 mm Hg
(C) 29.5 mm Hg (D) 28.8 mm Hg

Sol. (B)

P = 0.9 × 40 = 36 mm Hg

69. Water is added to the solution **M** such that the fraction of water in the solution becomes 0.9. The boiling point of this solution is

(A) 380.4 K (B) 376.2 K
(C) 375.5 K (D) 354.7 K

Sol. **(B)**

$$\Delta T_b = K_b \times m$$

$$= 0.52 \times \frac{0.1}{0.9 \times 18} \times 1000 = 3.2\ K$$

$T_b = 373 + 3.2 = 376.2\ K$