IITJEE 2008 Chemistry

Paper 1 Code 2

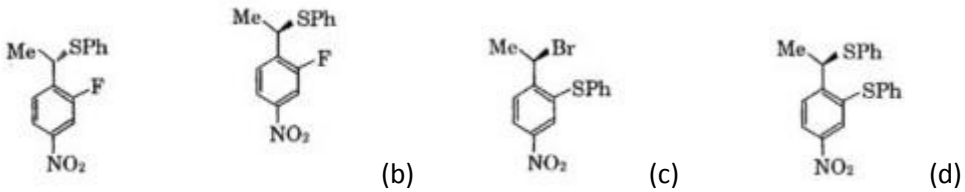
SECTION – I

Straight Objective Type

This section contains 6 multiple choice questions. Each question has 4 choices

(A) , (B) , (C) , (D) out of which **ONLY ONE** is correct .

47. The major product of the following reaction is

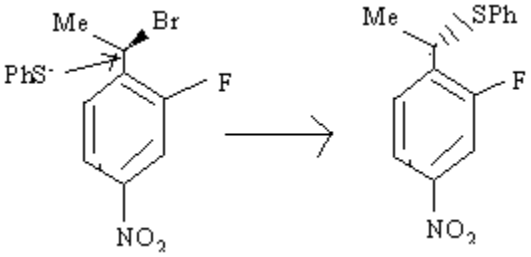


(a) (b) (c) (d)

Solution: PhS^- is a strong Na^- (also, note the presence of aprotic solvent

=> SN^2 will occure leading to inversion(Walden)

- F can not be substituted by PhS^- at $-NO_2$ is present at the "m" position



48. Hyperconjugation involves overlap of the following orbitals

(a) $\sigma - \sigma$ (b) $\sigma - P$ (c) $P - P$ (d) $\pi - \pi$

Solution: (B)

By the definition of hyper conjugation, it involves the overlap of σ & P orbital

49. Aqueous solution of $Na_2S_2O_3$ on reaction with Cl_2 gives

(a) $Na_2S_4O_6$ (b) $NaHSO_4$(c) NaCl (d) NaOH

Solution: (B)

$$Na_2S_2O_3 + 9H_2O + 7Cl_2 \rightarrow 2NaHSO_4 + 14HCl + H_2SO_4$$

50. Native silver metal forms a water complex with a dilute aqueous solution of NaCN in the presence of

(A) nitrogen (B) oxygen (C) carbon dioxide (D) argon

Solution: (B)

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

51. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base $\left(K_b = 1\times10^{-12}\, at 25^\circ C\right)$ is titrated with $\frac{2}{15}$ M HCl in water at 25 °C. The concentration of H^+ at equivalence point is $\left(K_w = 1\times10^{-14}\, at 25^0 C\right)$

(A) $3.7\times10^{-13}\, M$ (B) $3.2\times10^{-7}\, M$

(C) $3.2\times10^{-2}\, M$ (D) $2.7\times10^{-2}\, M$

Solution: (D)

Calculate the vol. of HCl to reach the equivalence point.

$$\Rightarrow 2.5\times\left(\frac{2}{5}\times1\right) = \left(\frac{2}{15}\times1\right)V_{HCl} \Rightarrow V_{HCL} = 7.5ml$$

=> net vol of solution at the equation point = V_{base} + V_{HCl} =2.5 + 7.5 = 10 ml

$$\Rightarrow \left[salt\right] = C = \frac{\frac{2}{5}\times2.5}{10} = 0.1M$$

$$pH = 7 - \frac{1}{2}\left(PK_b + \log_{10} C\right) = 1.5 \ ; \ (PK_b = 12)$$

$$\Rightarrow \left[H^+\right] = 10^{-1.5} = \frac{1}{10\sqrt{10}} \approx 3.2\times10^{-2}\, M$$

please note the above solution is incorrect(why?)

$pH = 7 - \frac{1}{2}\left(PK_b + \log_{10} C\right)$ is applicable only when $1 - h \approx 1$

here $h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_b C}} = \sqrt{\frac{10^{-14}}{10^{-12} \times 0.1}} \Rightarrow 1 - h \neq 1$

go basics to the basics

$B^+ + H_2O \rightleftharpoons BOH + H^+$

c

c - ch ch ch

$$\Rightarrow K_h = \frac{[BOH][H^+]}{[B^+]} = \frac{ch.ch}{c - ch}$$

$$\Rightarrow 10^{-2} = \frac{K_w}{K_b} = K_h = \frac{[H^+]^2}{c - [H^+]} \qquad \therefore c = 0.1$$

$$\Rightarrow [H^+] = -10^{-2} + \sqrt{10^{-4} + 4 \times 10^{-3}} = 2.7 \times 10^{-2} M$$

52. Under the same reaction condition, 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 $\frac{k_1}{k_0}$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction 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

Solution: (A)

first order: half life: $t_{1/2} = \frac{\ln 2}{k_1} = 40 \Rightarrow k_1 = \frac{\ln 2}{40} = \frac{0.693}{40}$

zero order: half life: $t_{1/2} = \frac{c_0}{2k_2} = 20 \Rightarrow k_2 = \frac{c_0}{40} = \frac{1.386}{40}$

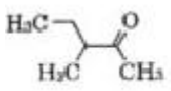
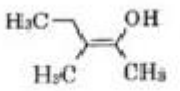
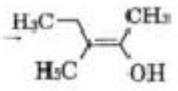
$$\Rightarrow \frac{k_1}{k_2} = \frac{1}{2}$$

SECTION - II

Multiple Correct Answers Type

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

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

(E) (F) (G)

(A) E, F and G are resonance structures

(B) E, F and K, G are tautomers

(C) F and G are geometrical isomers

(D) F and G are diastereomers

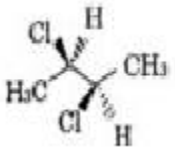
Solution: (B,C,D)

F is clearly the tautomer (enol form) of E

G is Geometric isomer(trans form) of F

=> E & G are also tautomers (geometric isomers are also diastereomers

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



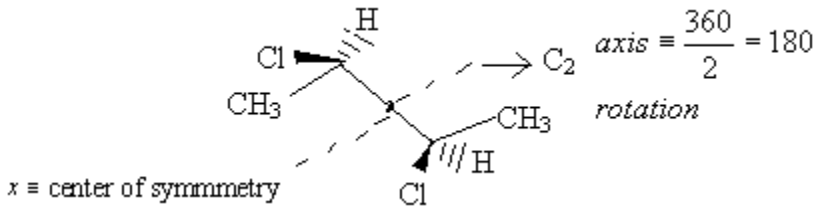
(A) The compound is optically active

(B) The compound possesses centre of symmetry

(C) The compound possesses plane of symmetry

(D) The compound possesses axis of symmetry

Solution:



center of symmetry: for every atom with coordinates x, y, z there exists a similar atom with coordinate -x, -y, -z with inversion center being the origin of the coordinates.

Plane of symmetry: plane which divides the molecule into halves which are mirror image of each other.

Axis of symmetry: If a molecule is rotated about an imaginary axis by an angle of $360^{o}/n$ & arrives at an arrangement indistinguishable from the original, the axis is n - fold axis of symmetry.

55. A gas described by van der Waals equation

(A) Behaves similar to an ideal gas in the limit of large molar volumes

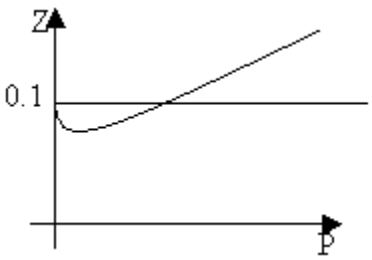
(B) Behaves similar to an ideal gas in the limit of large pressures

(C) Is characterized by van der walls coefficients that are dependent on the identity 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

Solution: (A, C, D)

$\left(P+\frac{a}{V_m^2}\right)\left(V_m-b\right)=RT$ (wander waals equation)



$when V_m \to l\arg e \Rightarrow P \to 0 \Rightarrow z \to 1$

As $p \to l \arg e \Rightarrow z > 1 \Rightarrow$ deviation from ideal gas

a, b are the characteristic constants of a real gas(independent of T)

since there are attractive forces between gas molecules, real gas pressure is always less than ideal gas pressure.

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) $(NH_4)_2SO_4$

Solution: (A, B)

Note: all of the given components: NH_4OH; NH_4NO_2; NH_4Cl; $(NH_4)_2SO_4$ will react with NaOH to give NH_3 gas.

Only NH_4NO_3 & NH_4NO_2 will react with Zn to give NH_3 gas.

$$NH_4NO_3 + 4Zn + 8NaOH \rightarrow 4Na_2ZnO_2 + 2NH_3 + 3H_2O$$

$$Nh_4NO_2 + 3Zn + 6NaOH \rightarrow 3Na_2ZnO_2 + 2NH_3 + 2H_2O$$

SECTION - III

Reasoning Type

This section contains 4 reasoning type questions. Each question has 4 choices

(A) , (B) , (C) , (D), out of which **ONLY ONE** is correct

57. STATEMENT-1: The plot of atomic number (y-axis) versus number of neutrons

(x-axis) for stable nuelei shows a curvature towards x-axis from the line of 45^0 slope as the atomic number is increased.

And

STATEMENT-2: Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides

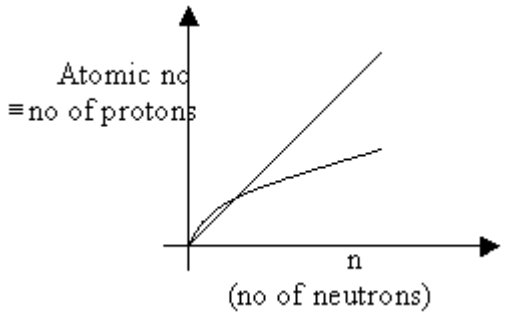
(A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1

(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 False

Solution: (B)



I_n heavy nuclei's n/p ratio > 1

As Z increases, attractive nuclear tends to saturate (saturation property of nuclear force) and after this, proton-proton repulsion tends to dominate leading to $E_n \Downarrow$

58. 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

STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 **is** a correct explanation for STATEMENT-1

(A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is a correct explanation for STATEMENT-1

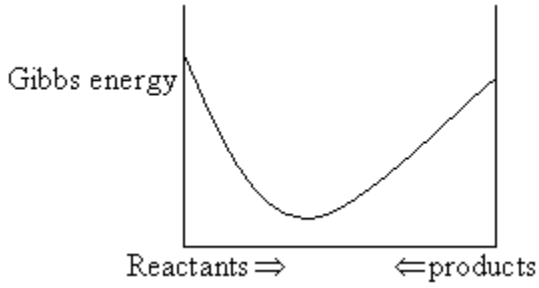
(B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 **is NOT** a correct explanation for STATEMENT-1

(C) STATEMENT-1 is True, STATEMENT-2 is False

(D) STATEMENT-1 is False, STATEMENT-2 is False

Solution: (D)

for a chemical reaction at equilibrium $\Delta G^0 \neq 0$ but $\Delta G = 0$ reactants & products to achieve minimum gibbs energy



59. STATEMENT-1: Bromobenzene upon reaction with Br2/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.

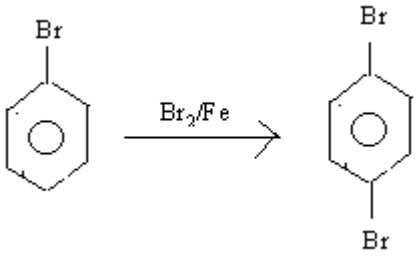
(A) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 **is** a correct explanation for STATEMENT-1

(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 False

Solution: (C)



(true)

-Br is weakly -O, p directing group due to +me effort. Inductive effect (-I) of halogens is stronger then their +M effect. This makes halogens as weakly deactivating group but incoming electrophile is directed to 'O' & 'P' position because of +Me effect though this effect is weakand.

60. STATEMENT-1: Pb^{2+} 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** a 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 False

Solution: (B)

$Sn^{4+}$is max stable than SN^{2} [SN^{2+} ions in the solution are good reducing agents]

$Pb2^{+}$ is more stable than Pb^{4+} $\left[PbCl_4 \xrightarrow{roomT} PbCl_2 + Cl_2\right]$

=> Pb^{4+} compounds are stranger oxidizing agents than Sn^{4+} (true)

As we move down the "C" group, higher oxidation state (+4) becomes more stable due to "inert-pair" effect but Pb is an exceptional case. (true)

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) ,(D) ,out of which **ONLY ONE** is correct .

Paragraph for Question Nos. 61 to 63

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 (K_f^{water}) = 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.

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

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

62. 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

63. Water is added to the solution **M** such that the mole 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

Solution: 61 (D)

Note; $X_{Ethanol}$ = 0.9(solvent); X_{water} = 0.1 (solute) $\left(\equiv X_B\right)$

$$\Delta T_f = K_f m(ethonal) = 2 \times \frac{X_B}{1 - X_B} \times \frac{1000}{M_A} = 2 \times \frac{0.1}{0.9} \times \frac{1000}{46} = 4.8k$$

=> freezing point of solution = 155.7 - 4.8 = 150.9 k

Solution: 62 (B)

To get vapour pressure of the solution M:

$$P_{total} = P_A^0 X_A = 40 \times 0.9 = 36 mmHg$$

[note: wter is assumed to be non – volatile]

as assumed in the question comprehension

Solution: 63(B)

$X_{Ethanol}$ = 0.9(solute); X_{water} = 0.1 (solvent)

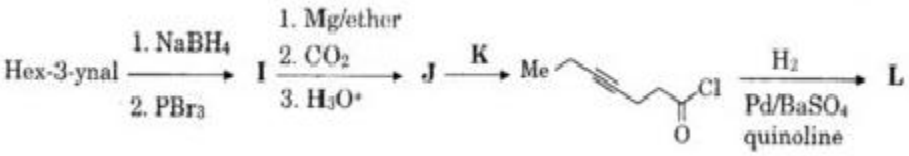
$$\Rightarrow \Delta T_b = K_b m(water) = K_b \times \frac{X_B}{1 - X_B} \times \frac{1000}{M_A}$$

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

$$\Rightarrow (T_b) = 100^0 C + 3.2 = 376.2k$$

Paragraph for Question Nos. 64 to 66

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



64. The structure of the product **I** is

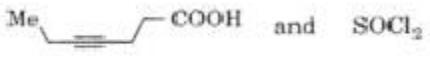
(A) 

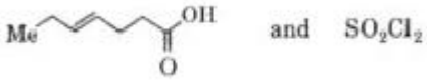
(B) 

(C) 

(D) 

65. The structure 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

66. The structure of the product **L** is

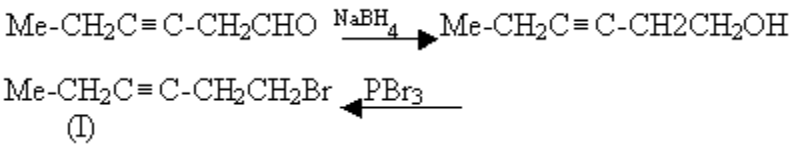
(A) 

(B) 

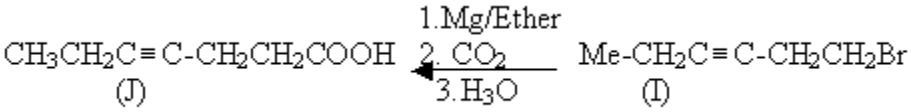
(C) 

(D) 

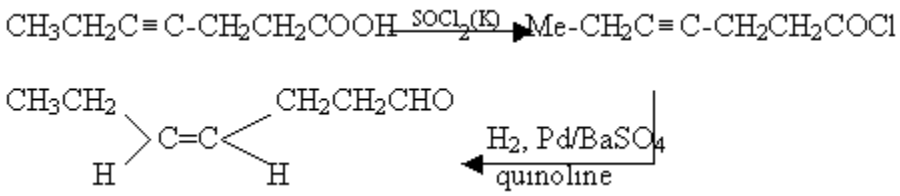
Solution: 64 (D)



Solution: 65 (A)



Solution: 66 (C)



Paragraph for Question Nos. 67 to 69

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 if NH_3 and PH_3. Phosphine is a flammable gas and is prepared from white phosphorous.

67. 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

68. Among the following, the correct statement is

(A) Between NH_3 and PH_3, NH_3 is a 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 a 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 a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

69. 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

Solution: 67(C)

Microbes will reduce nitrates in earth's crust. So, nitrates are less abundant in earth's crust.

Solution: 68(C)

NH_3 is stronger electron pair donor because N -atom is having the smaller size & electron density of the ion pair of e^-s present in one of the SP^3 hybrids on N - atom is more concentrated over a smaller region.

Solution: 69(B)

$$3NaOH + P + 3H_2O \rightarrow 3NaH_2PO_2 + PH_3$$

(Disproportionation reaction)