

Date: 14.10.2019

[Time : 3 Hours

[Total Marks : 100

Please check whether you have got the right question paper.

N.B. : 1. All Questions are compulsory.

2. Figures to the right indicate full marks.

3. Use of log-table/nonprogrammable calculator is allowed.

4. Answers for the same question as far as possible should be written together.

1. (A) Select the correct option and complete the following sentences. (any twelve) 12
- (i) Vant Hoff's reaction isochore gives the variation of -----with temperature  
a) Fugacity (b) activity (c) Equilibrium constant
- (ii) The equation  $\Delta G^0 = -RT \ln k$  is known as  
(a) Gibbs Helmholtz (b) Vant Hoff's isochore (c) Vant Hoff's isotherm
- (iii) The measure of extent of deviation from ideal behaviour is expressed by  
(a) activity (b) fugacity (c) activity coefficient
- (iv) The correct form of Gibbs Duhem equation is given by  
(a)  $\sum \mu_i n_i = 0$  (b)  $\sum \mu_i dn_i = 0$  (c)  $\sum n_i d\mu_i = 0$
- (v) Equivalent conductance is expressed by  
(a)  $\text{Scm}^{-1}\text{eq}^{-1}$  (b)  $\text{Scm}^2\text{eq}^{-1}$  (c)  $\text{S}^{-2}\text{m}^{-1}\text{eq}$
- (vi) Sum of transport numbers of an cation and anion is equal to  
(a) zero (b) one (c) 0.5
- (vii) NaCl has \_\_\_\_\_ structure.  
(a) FCC (b) BCC (c) HCP
- (viii) Coordination number of Cl<sup>-</sup> in CsCl is \_\_\_\_\_.  
(a) 4 (b) 6 (c) 8
- (ix) Third improvement suggested by Heitler and London to explain hydrogen molecule is \_\_\_\_\_.  
(a) ionicity (b) exchange (c) resonance
- (x) BCl<sub>3</sub> can be an example for \_\_\_\_\_.  
(a) equivalent hybrid orbitals (b) non equivalent hybrid orbitals  
(c) non hybrid orbitals
- (xi) Subtraction of wave function results \_\_\_\_\_.  
(a) bonding orbital (b) anti bonding orbital  
(c) non bonding orbital
- (xii) As per molecular orbital theory, H<sub>2</sub><sup>+</sup> is \_\_\_\_\_.  
(a) paramagnetic (b) diamagnetic (c) ferromagnetic
- (xiii) Reduction of ketone using NaBH<sub>4</sub> gives \_\_\_\_\_.  
(a) primary alcohol (b) secondary alcohol (c) tertiary alcohol
- (xiv) S<sub>N</sub><sup>i</sup> reaction taking place at chiral carbon atom leads to \_\_\_\_\_.  
(a) racemization (b) inversion of configuration (c) retention of configuration
- (xv) Phenoxide is stabilized by \_\_\_\_\_.  
(a) hydrogen bonding (b) resonance (c) inductive effect
- (xvi) Reaction of phenylmagnesium bromide with ethylene oxide gives \_\_\_\_\_.  
(a) 1-Phenylethanol (b) 2-Phenylethanol (c) Ethyl phenyl ether

- (xvii) Formation of \_\_\_\_\_ is not possible in the reaction of p-Bromotoluene with  $\text{NaNH}_2$  in liquid ammonia.  
 (a) o-Methyl aniline (b) m-Methyl aniline (c) p-Methyl aniline
- (xviii) Role of diethyl ether in the preparation of Grignard reagent is as a \_\_\_\_\_.  
 (a) catalyst (b) stabilizer (c) reagent

- (B) State whether the following statements are true or false. (any **three**) 3
- (i) Activity coefficient of electrolyte solution is always less than unity  
 (ii) For strong electrolytes degree of dissociation is nearly equal to one  
 (iii) Ionic bond is non directional bond.  
 (iv) More canonical forms means more stability to the molecule  
 (v) Alcohols are more acidic than phenols.  
 (vi)  $\text{SN}^1$  reaction at chiral carbon atom leads to racemization.

- (C) Match the column. (any **five**) 5
- |                        |                                  |
|------------------------|----------------------------------|
| (i) Fugacity           | (a) NaCl                         |
| (ii) Resistance        | (b) Does not exist               |
| (iii) AB type compound | (c) Reciprocal of conductance    |
| (iv) $\text{Ne}_2$     | (d) Intermolecular hydrogen bond |
| (v) Ethyl alcohol      | (e) $\text{Na}_2\text{O}$        |
| (vi) Salicylaldehyde   | (f) $\mu = \mu^0 + RT \ln f$     |
|                        | (g) Ionic bond                   |
|                        | (h) Intramolecular hydrogen bond |
|                        | (i) $l/a$                        |

2. Attempt any **four** of the following. 20
- (A) What is chemical potential? Derive Gibbs Duhem equation and explain its significance  
 (B) For the reaction  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{SO}_3(\text{g})$  equilibrium constant is 42.9 at 900 K. Calculate the standard free change  $\Delta G^0$  for the reaction at 900 K ( $R = 8.314 \text{ J deg}^{-1} \text{ mol}^{-1}$ )  
 (C) Explain the terms i) Fugacity ii) Activity  
 (D) Starting with  $\Delta G^0 = -RT \ln k$  Derive Van't Hoff's reaction isochore  
 (E) What is transport number of an ion? Describe moving boundary method for the determination of transport number of an ion  
 (F) How will you determine solubility and solubility product of sparingly soluble salts by Kohlrausch law of independent migration of ions?

3. Attempt any **four** of the following. 20
- (A) List various types of ionic crystals. Explain with suitable example any one among them.  
 (B) Define lattice energy. Write Born-Landé equation. Explain the terms involved it.  
 (C) With suitable examples explain formal charge.  
 (D) With the help of potential energy curve, explain any two improvements.  
 (E) Draw a neat and well labelled molecular orbital diagram of  $\text{F}_2$  molecule. Find its bond order. Predict its magnetic moment.  
 (F) With suitable example explain  $\text{sp}^2$  hybridisation.

4. Attempt any **four** of the following.
- (A) Explain the mechanism and stereochemistry of  $SN^1$  reaction with suitable example. **5**
- (B) What is cine substitution? Give the mechanism of reaction of chlorobenzene with  $NaNH_2$  in liquid  $NH_3$ . **5**
- (C) i) What are Grignard reagents? How are they prepared? What is the action of water on ethylmagnesium bromide? **3**  
 ii) Give the reaction of ethyllithium on solid carbon dioxide?. **2**
- (D) Explain the effect of hydrogen bonding on boiling point and water solubility of compounds? **5**
- (E) Give ring opening reactions of ethylene oxide by reaction with (i) ammonia (ii) Sodium ethoxide. **5**
- (F) How will you convert **5**  
 i) Cumene to phenol  
 ii) Benzenemetadisulphonic acid to resorcinol  
 iii) Phenol to anisole? Give chemical reactions.
5. Attempt any **four** of the following. **20**
- (A) Explain the variation of molar conductance with concentration for strong and weak electrolytes
- (B) Show that  $\left(\frac{\delta G}{\delta P}\right)_T = V$
- (C) Calculate the lattice energy of NaCl crystal from the following data by the use of Born-Haber cycle.
- |                                 |                              |
|---------------------------------|------------------------------|
| Heat of atomisation of sodium   | = 108.7 kJmol <sup>-1</sup>  |
| Heat of atomisation of chlorine | = 120.9 kJmol <sup>-1</sup>  |
| Ionisation potential of sodium  | = 493.7 kJmol <sup>-1</sup>  |
| Electron affinity of chlorine   | = -365.3 kJmol <sup>-1</sup> |
| Heat of formation of NaCl       | = -410.9 kJmol <sup>-1</sup> |
- (D) Draw a molecular orbital diagram of  $O_2$  molecule. Write its electronic configuration. Predict its magnetic property.
- (E) What are the factors that affect  $SN^1$  and  $SN^2$  reactions? Explain any two of them.
- (F) Give chemical reactions for the following conversions.
- i) Chlorobenzene to phenol
  - ii) Bromobenzene to phenyllithium
  - iii) Cyclohexanol to cyclohexene
  - iv) Phenol to p-Bromophenol
  - v) Ethylene to ethylene oxide

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