

[Time: Three Hours]

[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. The use of log-table/nonprogrammable calculator is allowed
4. Answers for the same question as far as possible should be written together

Q.1 (A)

Select the correct option and complete the following sentences  
(any twelve)

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- The escaping tendency of real gases is represented by \_\_\_\_  
(a) Entropy (b) Fugacity (c) activity
- If  $\Delta G^\circ$  for a reaction is greater than zero then K is \_\_\_\_  
(a) 0 (b)  $>1$  (c)  $<1$
- For a pure substance, chemical potential is equal to \_\_\_\_ /mol.  
(a) entropy (b) enthalpy (c) free energy
- Degree of ionization of an electrolyte depends on \_\_\_\_  
(a) Only nature of electrolyte (b) only presence of other ions (c) both
- The SI unit of cell constant is \_\_\_\_  
(a) cm (b)  $S\ m^{-1}$  (c)  $m^{-1}$
- If a transport number of  $K^+$  is 0.492 in KCl solution. The transport number of  $Cl^-$  ion will be \_\_\_\_  
(a) 0.840 (b) 0.508 (c) 0.492
- Geometry of  $SF_4$  molecule is \_\_\_\_  
(a) tetrahedral (b) distorted tetrahedral (c) octahedral
- Kapustinskii equation is used to calculate \_\_\_\_ energy.  
(a) Lattice (b) ionisation (c) Dissociation
- Bond order in  $O_2$  molecule is \_\_\_\_  
(a) 2 (b) 1 (c) 0
- NaCl crystal is of \_\_\_\_ type of crystal system.  
(a) Tetragonal (b) Monoclinic (c) Cubic
- The three equatorial chlorine atoms in  $PCl_5$  molecule are at \_\_\_\_ with respect to each other.  
(a)  $102^\circ$  (b)  $120^\circ$  (c)  $90^\circ$
- Coordination number of each ion in NaCl crystal is \_\_\_\_  
(a) 4 (b) 8 (c) 6
- Alcohols react with Grignards reagent forming \_\_\_\_  
(a) alkenes (b) alkanes (c) alkynes
- The phenoxide anion occurs in \_\_\_\_ canonical forms  
(a) five (b) four (c) three
- Alkyl lithium reacts with formaldehyde in presence of ether to form a product which on hydrolysis forms \_\_\_\_  
(a) aldehyde (b) carboxylic acid (c) primary alcohol

- (xvi) Cine substitution is observed in \_\_\_\_\_ mechanism.  
 (a)  $SN^1$  (b) benzyne (c)  $SN^2$
- (xvii) Phenyl magnesium chloride on treatment with water forms \_\_\_\_  
 (a) phenol (b) benzene (c) chlorobenzene
- (xviii) Elimination addition mechanisms are possible in the presence of \_\_\_\_\_.  
 (a) strong nucleophile (b) strong electrophile  
 (c) weak nucleophile

(B) State whether the following sentences are True or False(**any three**) 03

- (i) For strong electrolytes degree of dissociation is nearly equal to one.  
 (ii) Activity coefficient is always less than one  
 (iii) Lesser the number of resonating structures, the greater is stability of molecule.  
 (iv) The regular geometry for  $sp^3d^2$  type of hybridisation is square pyramidal.  
 (v)  $SN^1$  reactions are favoured by less polar solvents.  
 (vi) Dows process is the method used for preparation of phenol from Sodium phenoxide and alkyl halide

(C) Match the following(**any five**) 05

Column X		Column Y	
(i)	Chemical potential	(a)	endothermic
(ii)	Resistance	(b)	Epoxide
(iii)	Ionization energy	(c)	bond angle $107^\circ$
(iv)	Ammonia	(d)	Butanoic acid
(v)	$C_4H_9Li + CO_2$ and acidic hydrolysis	(e)	intensive property
(vi)	Three membered ring with oxygen	(f)	glycol
		(g)	Reciprocal of conductance
		(h)	Pentanoic acid

Q.2

Attempt **any four** of the following.

- (A) Derive Gibbs Duhem equation. 05
- (B) The equilibrium constant for a gaseous reaction is 170 at 500 K and its heat of reaction is  $-42.676 \text{ kJ}$ . Calculate equilibrium constant at 700 K. ( Given  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  ) 05
- (C) Explain variation of free energy with temperature and pressure. 05
- (D) Discuss the determination of solubility and solubility product of sparingly soluble salt by conductometric method. 05
- (E) What do you mean by limiting molar conductance? How is it determined for strong and weak electrolyte? 05



- (F) In the moving boundary method, for determination of transport number of potassium ions in  $0.1 \text{ mol dm}^3$  of potassium chloride the boundary moved through a distance of  $7.2 \text{ cm}$  in a tube of the cross sectional area of  $0.112 \text{ cm}^2$ . A current of  $0.0065$  amperes passed for  $2400$  seconds was responsible for the movement of the boundary. Calculate the transport number of  $\text{K}^+$  ion. ( $F=96500 \text{ c/mol}$ ) 05

Q.3

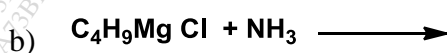
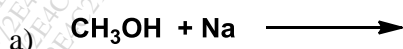
Attempt **any four** of the following

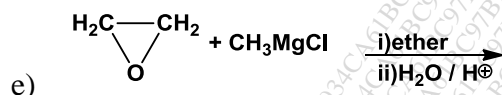
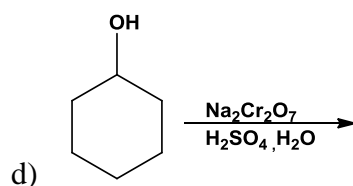
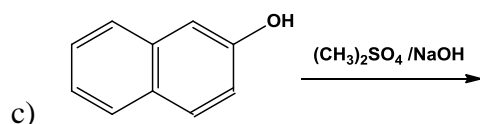
- (A) Define the terms: i.  $\sigma$  molecular orbital ii. Resonance iii. Hybridisation. Explain any one in detail. 05
- (B) Draw molecular orbital diagram of  $\text{B}_2$  molecule. calculate its bond order and state magnetic property. 05
- (C) Explain the shape of  $\text{XeF}_4$  molecule on the basis of covalent bonding, 05
- (D) With suitable example represent Born –Haber cycle for the formation of ionic compound. Mention the energies involved in each step. 05
- (E) On the basis of LCAO method explain the formation of Bonding molecular orbital and Antibonding molecular orbital. 05
- (F) Find the electron affinity of iodine using Born Haber cycle with the help of following data 05
- Heat of formation of  $\text{NaI} = -287.9 \text{ kJ/mol}$ , Heat of sublimation of sodium  $= 108.4 \text{ kJ/mol}$ , Heat of atomisation of iodine  $= 106.6 \text{ kJ/mol}$ , Ionisation energy of sodium  $= 493.8 \text{ kJ/mol}$ , Lattice energy of  $\text{NaI} = -690.8 \text{ kJ/mol}$

Q.4

Attempt **any four** of the following

- (A) What is elimination addition mechanism ? Give the mechanism of action of sodamide ( $\text{NaNH}_2$ ) in liquid ammonia on chlorobenzene. 05
- (B) How will you obtain phenol from Benzene sulphonic acid ? Why is phenol a weak acid ? What will be the products formed when phenol is treated with  
i) dil  $\text{HNO}_3$   
ii)  $\text{CH}_3\text{COCl}$  05
- (C) What is an organo metallic compound ? How will you synthesize the following, give any one method  
a) Phenyl Lithium  
b) Butyl magnesium bromide  
Why are both the compounds given above prepared under anhydrous conditions ? Explain 05
- (D) Complete the following reactions :- 05





(E) What are alcohols ? How are they classified ? Give examples. 05

From ethanol how will you prepare the following , giving reactions only

- i) ethylene
- ii) diethyl ether

(F) How will you synthesize the following , giving reactions only :- 05

- (a) Acetic acid from Ethanol
- (b) Ethylene oxide from ethylene chlorohydrin
- (c) Sodium phenoxide from Phenol
- (d) Triethanol amine from ethylene oxide
- (e) Methyl chloride from methanol

Q.5

Attempt **any four** of the following

(A) Derive an expression for Van't Hoff's reaction isotherm. 05

(B) What do you mean by a cell constant of a conductivity cell?  
How is it determined experimentally? 05

(C) Give an account of corrections applied to  $H_2$  molecule with respect to bond energy determination. 05

(D) Justify:- Beryllium molecule is not expected to exist according to molecular orbital theory. 05

(E) Explain the mechanism of alkaline hydrolysis of methyl bromide giving the energy profile diagram and stereochemistry of the products formed. 05

(F) How will you convert the following :- 05

- (a) Ethylene oxide to ethylene cyanohydrin
- (b) Phenol to picric acid
- (c) Methyl magnesium bromide to acetone
- (d) Methyl chloride to methyl lithium
- (e) Methanol to methyl acetate

xxxxxxx