[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: **12**
(attempt **any twelve**)

(i) Gibss free energy 'G' is _____ and a state function.
a) an intensive property b) an extensive property
c) colligative property

(ii) _____ Helmholtz free energy (A) in any process at constant temperature gives the maximum work done by the system.
a) increase in the b) decrease in the c) constant

(iii) The variation of equilibrium constant with temperature is given by _____ equation.
a) Gibbs-Helmholtz b) Van't Hoff isotherm c) Van't Hoff isochore

(iv) Specific conductance of a solution is the conductance offered by unit _____ of a solution.
a) volume b) density c) temperature

(v) Partial molal property is applicable to _____
a) open system b) isolated system c) closed system

(vi) The SI unit for conductivity cell constant is _____
a) m^{-1} b) cm^2 c)cm^{-1}

(vii) Crystal structure of CsCl is _____ .
a) fcc b) bcc c) hcp

(viii) In an ionic crystal cations and anions are held together by
a) electrostatic forces b) nuclear forces c) covalent bonds

(ix) In the formation of a molecule by an atom
a) only attractive forces operate b) only repulsive forces operate c) both attractive and repulsive forces operate

(x) Bond angle in a molecule adopting a trigonal planar geometry is _____ .
a) 180° b) 109.5° c) 120°

(xi) Elements with larger electronegativity difference combine to form
a) Ionic compound b) covalent compound c) metallic crystal

(xii) The bond order in O_2^+ is
a) 1.5 b) 2.5 c) 2

(xiii) Epoxide contains -------membered ring.
a) three b) four c) five

(xiv) Action of sodamide in liq.ammonia on p-bromo toluene gives-------
a) P-amino toluene b) m-amino toluene
c) mixture of p-amino toluene and m-amino toluene.

(xv) Organolithium compound reacts with alcohol to form--------
a)alkane b)alkyl halide c) higher alkane

(xvi) Allyl aryl ethers on heating at about 200^0 C undergoes rearrangement reaction known as ----------
a) Claisen rearrangement b) Fries rearrangement
c) Kolbe's reaction

(xvii) ---------- is a Grignard reagent.
a) Methyl magnesium bromide b) n-butyl lithium
c) Diethyl zinc

(xviii) Alkenes on treatment with ---------- gives epoxide.
a) peroxy acid b) $K_2Cr_2O_7$ c) $KMnO_4$

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

(i) Fugacity is a measure of escaping tendency for an ideal gases
(ii) In electrolytic solution, the current is carried by electrons.
(iii) Molecular orbitals are polycentric.
(iv) N_2 molecule is paramagnetic in nature.
(v) Addtion -elimination mechanism involves Benzyne intermediate formation.
(vi) Isobutyl alcohol is a secondary alcohol.

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

	Column A		**Column B**
1)	Mass of a matter	a)	a) square pyramidal
2)	Fugacity	b)	inversion of configuration
3)	BCl_3	c)	retention of configuration
4)	IF_5	d)	epoxy ethane
5)	Ethlene oxide	e)	oxitane
6)	S_Ni reaction	f)	trigonal bipyramidal
		g)	planar triangle
		h)	$\mu = \mu^0 + RT \ln f$
		i)	tetrahedral
		j)	extensive property
		k)	detergent

Q.2 Attempt any **four** from the following—

A Explain the terms - **05**
i) Helmholtz Free energy ii) Gibbs free energy

B Derive thermodynamic expression for Van't Hoff's reaction isotherm. **05**

C The free energy change (ΔG) for a particular process is -140.5 kJ mol^{-1} at 303 K and - 137.5 kJ mol^{-1} at 313K. Calculate the enthalpy change (ΔH) for the process at 308 K. **05**

D Explain the variation of molar conductance of an electrolyte with the concentration. **05**

E Describe 'moving boundary method' for the determination of transport number. **05**

F When the conductance of 0.5M solution is measured with the help of a conductivity cell in which the electrodes are 1.2 cm apart having an area of cross section 1.1 cm^2 found to be 4 x 10^{-2} Sm^2mol^{-1}. Calculate molar conductance of the solution. **05**

Q.3 Attempt any **four** from the following—

A i) Differentiate between the terms lattice energy and heat of solvation. **02**

ii) What is Kapustinskii's equation? Using this equation, calculate the lattice energy of KCl with the help of following data. **03**
radius of K^+ = 138 pm ; radius of NO_3^{-1} =189 pm; constant C = 1.079×10^5

B i) Discuss the structure of NaCl with the help of diagram. **03**

ii) radii of Zn^{2+} and S^{2-} are 0.6Å and 1.84Å respectively. Predict the coordination number of Zn^{2+} and the crystal structure of ZnS. **02**

C Write notes on **05**
i) resonance ii) sigma and pi covalent bonds

D i) Mention the theoretical and experimental bond energy and bond lengths for the hydrogen molecule. **02**

ii) Explain the first improvement applied on the wave function of the hydrogen system to bring the theoretical values of bond energy and bond length closer to the experimental values. **03**

E i) Draw a neat labelled molecular orbital energy level diagram for N_2 molecule and give it's molecular electronic configuration. Comment on it's bond order and magnetic property. **05**

F i) Discuss the conditions required for the formation of molecular orbitals. **02**

ii) Explain the representation of bonding and anti-bonding molecular orbitals on the basis of wave function. **03**

Q.4 Attempt any **four** from the following—

A i) Distinguish between S_N1 and S_N2 reactions. **03**

ii) What is Grignard's reagent? Give its preparation. **02**

B i) What is etherification and sulphation of alcohols? Give one example each. **03**

ii) Explain— **02**
a) p-nitro phenol is more acidic than phenol.
b) o-nitro phenol is steam volatile whereas p-nitro phenol is not.

C Give preparation of phenyl lithium and what happens when phenyl lithium reacts with **05**
a)acetaldehyde b) CO_2/H_3O^+ c) ethylene oxide/H_2O

D What are primary, secondary and tertiary alcohols? Give one method of preparation of each of them. **05**

E i) Give preparation of phenol from **03**
a) chloro benzene by Dow's process
b) benzene sulphonic acid

ii) What happens when phenol reacts with **02**

a) dil HNO_3 b) excess of bromine water at room temp.

F i) Give preparation of ethylene oxide from **03**
a) ethane b) vicinal halohydrin

ii) How will you prepare following compounds from ethylene oxide. **02**
a) ethylene glycol b) 2-bromo ethanol

Q.5 Attempt any **four** from the following—

A Explain the variation of chemical potential with pressure and temperature. **05**

B The molar conductance of KBr at infinite dilution is 1.52×10^{-2} S m^2 mol^{-1} **05** and the transport number of K^+ is 0.48. Calculate the ionic mobility of the cation at infinite dilution of KBr at 298 K.

C Explain the following with the help of diagrams. **05**
i) geometry of BrF_3 molecule ii) sp^3d hybrid orbitals

D a) Write a note on gerade and ungerade orbitals. **03**
b) 'Hydrogen exists as diatomic molecule but Helium does not'. Justify on the basis of MOT. **02**

E What is Cine substitution; explain with mechanism. **05**

F What happens when- **05**
i) Phenol is treated with benzoyl chloride
ii) Sodium phenoxide is heated with ethyl bromide in ethanol.
iii) Phenyl lithium reacts with acetaldehyde followed by hydrolysis.
iv) Ethylene oxide reacts with HCN.
v) Phenyl magnesium bromide is treated with phenyl cyanide followed by hydrolysis.

****