[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**
(**any twelve**)

(i) The rate of change of free energy with temperature at constant pressure is _____ .
a) volume b) - ve entropy c) + ve entropy

(ii) Decrease in Gibbs free energy is _____ done.
a) maximum work b) net-work c) limited work.

(iii) Van't Hoff reaction isotherm is given as_____
a) $\Delta G = - RT \ln K$ b) $\Delta G = RT \ln K$ c) $\Delta G^o = - RT \ln K$

(iv) Specific conductance of a solution is the conductance offered by _____ volume of solution.
a) 0.1 dm^3 b) 1cm^3 c) 0.1 cm^3

(v) As the temperature increases, resistance of an electrolytic conductor _____
a) increases b) decreases c) does not get affected.

(vi) At the same temperature, the transport number of an ion will be _____ in solutions of different salts of the ion.
a) common b) different c) constant

vii) Among the following compounds, _____ is expected to be more ionic.
a) H_2O b) NaCl c) $SrCl_2$

viii) During the formation of a chemical bond, energy of the system _____ .
a) decreases b) increases c) does not change.

ix) The H — P — H bond angle in PH_3 is _____
a) $106^{0'}$ b) 94^0 c) 84^0

x) The number of lone pairs of electrons in NH_3 molecule is _____ .
(a) one (b) two (c) three

xi) The formal charge on H atom in $[PH_4]^{+1}$ ion is
a) +1 b) +2 c) 0

xii) The contributing structures of a molecule exhibiting resonance should have _____ number of unpaired electrons
a) different b) same c) neither a) nor b)

xiii) o- bromo toluene on treatment with sodamide in presence of liq. ammonia gives
a) o-amino toluene b) m-amino toluene
c) mixture of o-amino toluene & m-amino toluene.

xiv) Chiral alcohol reacts with thionyl chloride to form alkyl chloride is_____

a) S_N1 reaction b) $S_N2$reaction c) S_Ni reaction

xv) Phenols are_____

a) weakly acidic b) strongly acidic c) none of them.

xvi) Reaction of epoxide with HCN leads to formation of _____

a) alkyl cyanide b) cyanohydrin c) alcohol

xvii) Nitration of phenol with conc.HNO_3 gives -------

a) o-nitro phenol b) p-nitro phenol c) 2,4,6-nitro phenol

xviii) Reaction of ethylene oxide with Grignard reagent followed by acid hydrolysis gives ---------

a) secondary alcohol b) primary alcohol c) alkoxy alkane

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

(i) In electrolytic conductors, transfer of matter does not take place.

(ii) Chemical potential is the Gibbs free energy of 1 mole component present in system.

(iii) d orbitals are un-gerade in nature.

iv) BF_3 molecule has two lone pairs of electrons.

(v) Ethyl alcohol has lower boiling point than Dimethyl ether.

vi) p-nitrophenol is more acidic than phenol.

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

	Column A		**Column B**
1)	Fugacity	a)	Bent 'T' shaped
2)	Electronic conductors	b)	organo lithium compound
3)	BrF_3	c)	organo magnesium compound
4)	CH_4	d)	current carried by electrons
5)	Grignard reagent	e)	favoured by less polar solvent
6)	S_N2 reaction	f)	escaping tendeny
		g)	planar triangular
		h)	tetrahedral
		i)	favoured by weak nucleophile
		j)	S_N1 mechanism

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

A Derive Gibbs-Duhem equation. **05**

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

C Explain - whether the following process- **05**

CCl_4(liquid) + H_2 (gas) →HCl(gas) + $CHCl_3$ (liquid)

is spontaneous or non-spontaneous at 298 K under standard state of conditions. (Given - At 298K, ΔH^o = -91 kJ and ΔS^o = 41.5 JK^{-1} for this reaction.)

	D	i)	State Kolhrausch's law of independent migration of ion.	**05**
		ii)	The values of molar conductance at infinite dilution for sodium acetate, hydrochloric acid and sodium chloride are 0.00910, 0.04261 and 0.01264 S m^2 mol^{-1} respectively. Calculate the molar conductance of acetic acid at infinite dilution.	
	E		Define the terms – i) conductance, ii) specific conductance, iii) cell constant, iv) molar conductance and v) transport number.	**05**
	F		Describe the factors affecting the transport number.	**05**
Q.3			Attempt any **four** from the following—	
	A		Define following terms: a) heat of solution b) heat of hydration c) lattice energy.	**03**
			ii) How are these related to each other? How do they help in understanding the solubilities of ionic compounds?	**02**
	B		Give an account of the following: i) Born Lande's equation ii) Structure of CsCl	**05**
	C		What are the important postulates of 'Valence Bond Theory'?	**05**
	D		Predict the geometry and give an example for each one of the following molecules. i) AB_2 molecule with 1 lone pair of electrons. ii) AB_4 molecule with 2 lone pairs of electrons. iii) sp^3d^2 and sp^3d hybrid orbitals	**05**
	E		Draw a neat, labeled MO diagram for F_2 molecule. Calculate its bond order and mention its molecular configuration and magnetic property.	**05**
	F		Explain why mixing of orbitals takes place in case of B_2 and C_2 molecules. Give an account of the magnetic properties of B_2 and C_2 molecules on the basis of MOT.	**05**
Q.4			Attempt any **four** from the following—	
	A	(i)	Give preparation of phenol from- a) cumene b) chlorobenzene	**03**
		ii)	Explain the effect of electron donating substituent on acidic character of phenol giving one example.	**02**
	B		What is cine substitution? Explain with mechanism.	**05**
	C	(i)	What is the action of $K_2Cr_2O_7$/ conc. H_2SO_4 on a) Isopropyl alcohol b) n- Butyl alcohol c)t- butyl alcohol	**03**
		(ii)	Give preparation of ethylene oxide from a) ethene b) ethylene chlorohydrin	**02**
	D	(i)	Give preparation of phenyl magnesium bromide and what happens when phenyl magnesium bromide reacts with a) H_2O b) dry ice	**03**
		(ii)	What is sulphation of alcohol? Give one example.	**02**
	E		What happens when- a) cyclohexyl magnesium chloride reacts with ammonia. b) sodium phenoxide is heated with ethyl bromide in ethanol.	**05**

c) ethylene oxide is heated with excess of water in presence of H_2SO_4
d) phenol is treated with bromine water.
e) 2-propanol is heated with 60% H_2SO_4 at 170^0C
f) ethyl lithium reacts with ethanol.

F (i) What happens when ethylene oxide reacts with **03**
a) HBr b) NH_3 c) C_2H_5OH /dil.H_2SO_4

(ii) What is etherification of alcohol? Give one example. **02**

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

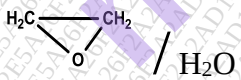
A Derive Gibbs-Helmholtz equation **05**

B The value of molar conductance at infinite dilution of $Al_2(SO_4)_3$ is 858 S cm^2/mol while that of SO_4^{2-} ions is 160 S cm^2/mol. Calculate the molar conductance of Al^{3+} ion at infinite dilution. **05**

C Explain the following ---
i) Equivalent and non-equivalent hybrid orbitals **03**
ii) Equatorial P— Cl bonds are shorter than the axial P— Cl bonds in PCl_5 molecule. **02**

D Answer the following with reference to MOT **05**
i) definition of molecular orbitals
ii) conditions for the formation of molecular orbitals in di atomic molecules
iii) formation of molecular orbitals with the help of diagrams.

E Explain the mechanism of alkaline hydrolysis of methyl bromide giving energy profile diagram. **05**

F What happens when methyl lithium reacts with **05**
i) C_2H_5Br
ii) CH_3CHO/H_3O^+
iii) CO_2/H_3O^+
iv) CH_3COCH_3/H_3O^+
v)  H_2O

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