D-P Code 54247
S.Y.B.Sc Paper I Sem III
26/3/2010
M.K.T

[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) $\Delta G^\circ = - RT \ln K$

(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 [illegible] hydrolysis gives ---------
a) secondary alcohol b) primary alcohol c) alkoxy alkane

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

(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) $\rightarrow$HCl(gas) + $CHCl_3$ (liquid)

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

3

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: 05

i) Born Lande's equation ii) Structure of CsCl

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. 05

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

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- 03

a) cumene b) chlorobenzene

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 03

a) Isopropyl alcohol b) n- Butyl alcohol c)t- butyl alcohol

(ii) Give preparation of ethylene oxide from 02

a) ethene b) ethylene chlorohydrin

D (i) Give preparation of phenyl magnesium bromide and what happens when phenyl magnesium bromide reacts with 03

a) H_2O b) dry ice

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

E What happens when- 05

a) cyclohexyl magnesium chloride reacts with ammonia.

b) sodium phenoxide is heated with ethyl bromide in ethanol.

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—

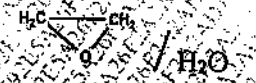
A Derive Gibbs-Helmholtz equation. 05

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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(5).

[Time: Three Hours]	**QP CODE 54247**	[Marks:100]
Semester III Paper I dated 26/03/2019		
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**
		(i)	-ve entropy			**1**
		(ii)	net work			**1**
		(iii)	$\Delta G^{\circ} = -RT \ln K$			**1**
		(iv)	$1cm^3$			**1**
		(v)	increases			**1**
		(vi)	different			**1**
		(vii)	NaCl			**1**
		(viii)	decreases			**1**
		(ix)	94^0			**1**
		(x)	one			**1**
		(xi)	0 (zero)			**1**
		(xii)	same			**1**
		(xiii)	Mixture of o-aminotoluene and m-amino toluene			**1**
		(xiv)	SN_1 reaction			**1**
		(xv)	Weakly acidic			**1**
		(xvi)	cyanohydrin			**1**
		(xvii)	2,4,6-trinitrophenol			**1**
		(xviii)	Primary alcohol			**1**
	B		State whether the following sentences are **True or False**			
		i)	False			**1**
		ii)	False			**1**
		iii)	False			**1**
		iv)	False			**1**
		(v)	True			**1**
		(vi)	False			**1**
	C		Match the column			
		(i)	Fugacity		Escaping tendency	**1**
		(ii)	Electronic conductors		Current carried by electrons	**1**
		(iii)	BrF_3		Bent 'T' shaped.	**1**
		(iv)	CH_4		tetrahedral	**1**
		(v)	Grignard reagent		Organo magnesium compound	**1**
		(vi)	SN^2 reaction		Favoured by less polar solvent	**1**
Q.2		A	Derive Gibbs-Duhem Equation.			
			Derive Gibbs-Duhem equation. **5**			

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Consider an open system consists of n_1, n_2, n_3, n_4, ... n_i number of moles of component 1, 2, 3, ..., i respectively. The free energy G of the system is an extensive property and is a function of various variables as-

i.e. $G = f(P, T, n_1, n_2, n_3, \ldots, n_i)$

The free energy change due to small change in pressure, temperature and amounts of various components can be given by-

$$dG = \left[\frac{dG}{dP}\right]_{T,N} dP + \left[\frac{dG}{dT}\right]_{P,N} dT + \left[\frac{dG}{dn_1}\right]_{T,P,n_2,n_3,\ldots n_i} dn_1 + \left[\frac{dG}{dn_2}\right]_{T,P,n_1,n_3,\ldots n_i} dn_2 + \cdots + \left[\frac{dG}{dn_i}\right]_{T,P,n_1,n_3,\ldots n_{i-1}} dni$$

and at constant temperature and pressure, the first two terms of the above equation becomes zero and the equation reduces to—

$$(dG)_{P,T} = \left[\frac{dG}{dn_1}\right]_{T,P,n_2,n_3,\ldots n_i} dn_1 + \left[\frac{dG}{dn_2}\right]_{T,P,n_1,n_3,\ldots n_i} dn_2 + \cdots + \left[\frac{dG}{dn_i}\right]_{T,P,n_1,n_3,\ldots n_{i-1}} dni$$

But we know that, the rate of change of free energy per mole is the chemical potential μ of that component, therefore above equation can also be written as-

$(dG)_{P,T} = \mu_1\, dn_1 + \mu_2 dn_2 + \cdots + \mu_i dni$ .....①

On integrating above equation, we get

$(dG)_{P,T} = \mu_1\, dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \cdots + \mu_i dni + n_i d\mu_i$

On rearranging the above equation-

$(dG)_{P,T} = \mu_1\, dn_1 + \mu_2 dn_2 + \cdots + \mu_i dni + n_1 d\mu_1 + n_2 d\mu_2 + n_2 d\mu_2 + n_i d\mu_i$ .....②

On substituting the value from equation ① in ②it reduces to

$$(dG)_{P,T} = (dG)_{P,T} + n_1 d\mu_1 + n_2 d\mu_2 + n_2 d\mu_2 + n_i d\mu_i$$

$$n_1 d\mu_1 + n_2 d\mu_2 + n_2 d\mu_2 + n_i d\mu_i = 0 \text{ .....③}$$
$$\text{or} \quad \sum n_i d\mu_i = 0 \text{ .....④}$$

Equation ③ and ④is called as Gibbs- Duhem equation.

B

Explain the variation of chemical potential with pressure and temperature.

5 mks

Variation of chemical potential w.r.t. pressure at constant temperature—

We know that, the chemical potential of the i^{th} component can be given as—

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,ni-1} \text{.....①}$$

Differentiating the above equation w.r.t. pressure at constant temperature, we get

$$\left(\frac{d\mu_i}{dP}\right)_{T,ni-1} = \left(\frac{d^2G}{dP dn_i}\right)_{T,ni-1} \text{.....②}$$

But, the rate of change of free energy w.r.t. pressure at constant temperature is equal to the volume of the system

i.e. $\left(\frac{dG}{dP}\right)_T = V$

differentiating the above equation w.r.t. n_i at constant T, P and n_{i-1}, we get

$$\left(\frac{d^2G}{dP dni}\right)_{T,ni-1} = \left(\frac{dV}{dn_i}\right)_{T,P,ni-1} = partial\ molal\ volume = \bar{V}$$

$$\therefore \left(\frac{d^2G}{dPdni}\right)_{T,,ni-1} = \bar{V} \ldots\ldots\ldots ③$$

Comparing equation ② and ③

$$\bar{V} = \left(\frac{d\mu_i}{dP}\right)_{T,ni-1}$$

Thus, the rate of change of chemical potential of the i^{th} component with pressure at constant temperature is equal to the partial molal volume of that constituent.

Variation of chemical potential w.r.t. pressure at constant temperature—

Similarly, by differentiating equation ① w.r.t. temperature at constant pressure, we get

$$\left(\frac{d\mu_i}{dT}\right)_{P,ni-1} = \left(\frac{d^2G}{dTdn_i}\right)_{P,ni-1} \ldots\ldots ④$$

But, we know that the rate of change of free energy w.r.t. temperature is equal to negative entropy of the component,

i.e. $\left(\frac{dG}{dT}\right)_P = -S$

Differentiating the above equation w.r.t. n_i at constant T, P and n_{i-1}, we get

$$\left(\frac{d^2G}{dTdni}\right)_{T,,ni-1} = -\left(\frac{dS}{dn_i}\right)_{T,P,ni-1} = partial\ molal\ entropy = \bar{S}$$

$$\therefore \left(\frac{d^2G}{dTdni}\right)_{P,ni-1} = \bar{S} \ldots\ldots\ldots ⑤$$

Comparing equation ④ and ⑤

$$-\bar{S}_i = \left(\frac{d\mu_i}{dT}\right)_{P,ni-1}$$

Thus, the rate of change of chemical potential of the i^{th} component with temperature at constant pressure is equal to the negative partial molal entropy of that constituent.

		C	$\Delta G^0 = \Delta H^0 - T\Delta S^0$ - 1 mks $= -91 - 298(41.5) = -12458$ KJ - 3mks i.e. spontaneous - 1 mks		
		D	i) Statement of Kolhrausch's law of independent of migration -2 mks ii) $CH_3COONa + HCl = CH_3COOH + NaCl$ 1 mks Substitution of corresponding values and correct calculation – 2mks		
		E	1mks -for Each definition		
		F	Factors affecting – a) concentration b) temperature c) hydration d) complex ion formation - 5 mks		
Q.3			Attempt **any four** of the following		
	A	i)	Definition of all the three terms – hydration energy, Heat of solution, lattice energy		**3 (1 mark each)**
		ii)	$\Delta H_{solution} = \Delta H_{solvation} + \Delta H_{lattice}$		**1**
			Explanation for the solubilities of ionic compounds on the basis of this equation.		**1**

	B		i) Born Lande's equation and the details of various terms involved in it .	2.5 marks
	C		ii) structural details of CsCl and diagram	2.5 marks
	D	i) ii) iii)	AB_2 molecule with lone pair of electrons AB_4 molecule with 2 lone pair of electrons } geometry and example of each type Sp^3d^2 and Sp^3d^2 hybrid orbitals Diagrams for all the geometries	1+1+1 +1 1
	E.		Neat, labelled molecular diagram of F_2 molecule Correct distribution of electrons Bond order, molecular configuration and magnetic property	2 marks 1.5 M 1.5 M
	F		Giving reason for mixing of orbitals in B_2 and C_2 molecules MO diagram for B_2 and C_2 molecules with explanation for magnetic properties	1.5 M 3.5 M
Q.4			Attempt **any four** of the following	
	A	(i)	Correct reaction for preparation -1.5 marks each.	3
		(ii)	Explanation with example -2 marks.	2
	B		Explanation with example -2 marks. Mechanism 3steps-1 mark each.	5
	C	(i)	Correct reaction -one mark each	3
	D	(i)	Preparation -1 mark. What happens when: correct reaction-1 mark each.	3
	D	(ii)	Explanation-1 mark. Example 1 mark.	2
	E		Correct reaction -1 mark each.	5
	F	(i)	Correct reaction one mark each.	3
		(ii)	Explanation-1 mark. Example-1 mark.	2
Q.5	A		Derive Gibbs-Helmholtz equation- Gibbs-Helmholtz equation gives the mathematical relation between free energy change ΔG, enthalpy change ΔH and rate of change of free energy with constant temperature. This equation is applicable to any physical or chemical change. We know that, the Gibbs free energy of a substance can be given as- $G = H - TS$ .....(1) But the enthalpy of the substance can be given as- $H = E + PV$ Therefore, equation (1) can be written as- $\therefore G = E + PV - TS$ On differentiating above equation we get, $dG = dE + PdV + VdP - TdS - SdT$ .....(2) But from 1st law of thermodynamics – $dq = dE + PdV$ and for reversible reaction $dq = TdS$ $\therefore TdS = dE + PdV$ On substituting the above values in equation (2), it becomes, $dG = TdS + VdP - TdS - SdT$ $\therefore dG = VdP - SdT$ At constant pressure, the term $VdP = 0$ Hence, $dG = -SdT$ .....(3)	5marks

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			Suppose, G_1 and G_2 are free energies of the system at initial and final state respectively and let dG_1 and dG_2 be the changes in the free energies when the temperature is changed by a very small amount say dT, Then, from equation (3), The change in free energy at initial state can be given as – $dG_1 = -S_1dT$ similarly, at final $dG_2 = -S_2dT$ $\therefore$ Change in free energy will be $dG_2 - dG_1 = -S_2dT - (-S_1dT)$ $\therefore d(G_2 - G_1) = -(S_2 - S_1)\,dT$ $d(\Delta G) = -\Delta S\,dT$ At constant pressure, $\left(\frac{d\Delta G}{dT}\right)_P = -\Delta S$ .....(4) Substituting the above value in equation (1), it becomes $$\Delta G = \Delta H + T\left(\frac{d\Delta G}{dT}\right)_P$$ The term $\left(\frac{d\Delta G}{dT}\right)_P$ is called as temperature coefficient, it can be defined as the rate of change of change in free energy with temperature at constant pressure, and the above equation is known as the Gibb's Helmholtz equation.	
	B		$\Lambda[Al_2(SO_4)_3] = 2\,\Lambda\,Al^{-3} + 3\,\Lambda\,SO_4^{-2}$ 3mks $858 = 2\,\Lambda\,Al^{-3} + 3(160)$ 2mks	
	C	i) ii)	Explanation for equivalent and non-equivalent hybrid orbitals with examples Reason for the difference in the bond lengths of equatorial and axial P— Cl bonds in PCl_5 molecule.	**3** **2**
	D		Definition of molecular orbitals Conditions for the formation of molecular orbitals	**2** **3**
	E		Explanation with reaction -2 marks. Mechanism -2marks, energy profile diagram-1mark.	**5**
	F		Correct reaction -1 mark each.	5