(1)

Q. P. Code :- 53460

Rajendra Laxman Pathare.

25th March 2019

Paper / Subject Code: 79508 / Chemistry - Paper -I

28/3/2019.

S. Y. Bsc Paper I Sem III AIKT

[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) 12

(i) The escaping tendency of real gases is represented by ____
(a) Entropy (b) Fugacity (c) activity

(ii) If ΔG° for a reaction is greater than zero then K is _____
(a) 0 (b) >1 (c) <1

(iii) For a pure substance, chemical potential is equal to ____/mol.
(a) entropy (b) enthalpy (c) free energy

(iv) Degree if ionization of an electrolyte depends on _____
(a) Only nature of electrolyte (b) only presence of other ions (c) both

(v) The SI unit of cell constant is ___
(a) cm (b) S m^{-1} (c) m^{-1}

(vi) 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

(vii) Geometry of SF_4 molecule is _____
(a) tetrahedral (b) distorted tetrahedral (c) octahedral

(viii) Kapustinskii equation is used to calculate_____ energy.
(a)Lattice (b)ionisation (c) Dissociation

(ix) Bond order in O_2 molecule is _____
(a) 2 (b)1 (c) 0

(x) NaCl crystal is of _____ type of crystal system.
(a) Tetragonal (b)Monoclinic (c)Cubic

(xi) The three equatorial chlorine atoms in PCl5 molecule are at_____ with respect to each other.
(a)102^0 (b)120^0 (c)90^0

(xii) Coordination number of each ion in NaCl crystal is_____
(a)4 (b)8 (c)6

(xiii) Alcohols react with Grignards reagent forming_____
(a) alkenes (b) alkanes (c) alkynes

(xiv) The phenoxide anion occurs in _____ canonical forms
(a) five (b) four (c) three

(xv) 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

C97BA73BF72E4C21E71C2EBE93929BD1

(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 angle107^0
(iv)	Ammonia	(d)	Butanoic acid
(v)	$C_4H_9I + CO_2$ 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

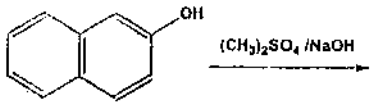
(B) The equilibrium constant for a gaseous reaction is 170 at 500 K and its heat of reaction is – 42.676 kJ. Calculate equilibrium constant at 700 K. (Given R = 8.314 J K^{-1} mol^{-1}) 05

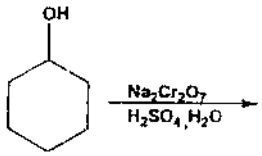
(C) Explain variation of free energy with temperature and pressure. 05

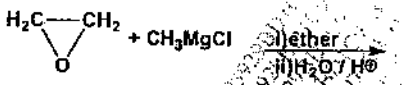
(D) Discuss the determination of solubility and solubility product of sparingly soluble salt by conductometric method. 05

(E) What do you meant 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 mol dm^3 of potassium chloride the boundary moved through a distance of 7.2 cm in a tube of the cross sectional area of 0.112 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 K^+ ion. (F=96500 c/mol)	05
Q.3		Attempt **any four** of the following	
	(A)	Define the terms: i.sigma(σ) molecular orbital ii.Resonance iii. Hybridisation. Explain any one in detail	05
	(B)	Draw molecular orbital diagram of B_2 molecule, calculate its bond order and state magnetic property	05
	(C)	Explain the shape of 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. Heat of formation of NaI = -287.9 kJ/mol, Heat of sublimation of sodium = 108.4 kJ/mol, Heat of atomisation of iodine= 106.6 kJ/mol, Ionisation energy of sodium= 493.8 kJ/mol, Lattice energy of NaI= -690.8 kJ/mol	05
Q.4		Attempt **any four** of the following	
	(A)	What is elimination addition mechanism ? Give the mechanism of action of sodamide ($NaNH_2$) 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. HNO_3 ii)CH_3COCl	05
	(C)	What is an organic metallic compound ? How will you synthesize the following, give any one method a) Phenyl Lithium b) n-Butyl magnesium bromide Why are both the compounds given above prepared under anhydrous conditions ? Explain	05
	(D)	Complete the following reactions :- a) $CH_3OH + Na \longrightarrow$ b) $C_4H_9MgCl + NH_3 \longrightarrow$	05

c) 

d) 

e) 

(E) What are alcohols ? How are they classified ? Give examples. From ethanol how will you prepare the following , giving reactions only — 05
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 meant by a cell constant of a conductivity cell? How is it determined experimentally? — 05

(C) Giv. 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

5

[Time: Three Hours] [Marks:100]

Semester III Paper I ATKT dated 25/03/2019 QP code: 53460

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)	**Fugacity**			
		(ii)	**one**			
		(iii)	Free energy			
		(iv)	Nature of electrolyte			
		(v)	m^{-1}			
		(vi)	0.508			
		(vii)	distorted tetrahedral			1
		(viii)	Lattice			1
		(ix)	2			1
		(x)	cubic			1
		(xi)	120°			1
		(xii)	6			1
		(xiii)	alkanes			1
		(xiv)	five			1
		(xv)	Primary alcohol			1
		(xvi)	benzyne			1
		(xvii)	benzene			1
		(xviii)	Strong nucleophile			1
	B		State whether the following sentences are True or False			
		(i)	false			
		(ii)	true			
		(iii)	false			
		(iv)	false			
		(v)	false			
		(vi)	false			1
						1
	C		Match the column			
		(i)	Chemical potential		Intensive property	
		(ii)	resistance		Reciprocal of conductance	
		(iii)	Ionization energy	(a)	Endothermic process	1
		(iv)	Ammonia	(c)	Bond angle 107°	1
		(v)	$C_4H_9Li+CO_2$ and acidic hydrolysis	(h)	Pentanoic acid	1
		(vi)	Three membered ring with oxygen	(b)	Epoxide	1

7

Q.2	A		**Derive Gibbs-Duhem equation.** 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. The free energy change due to small change in pressure, temperature and amounts of various components can be given by- and at constant temperature and pressure, the first two terms of the above equation becomes zero and the equation reduces to— 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- .....① On integrating above equation, we get On rearranging the above equation- .....② On substituting the value from equation ① in ②it reduces to .....③ or .....④ Equation ③ and ④is called as Gibbs- Duhem equation.	5 mks
	B		.....3 MKS Correct calculation .....2 mks	
	C		Correct derivation of the general eauation $dG = VdP - SdT$ from $G = H - TS$ 3 mks the condition a) at constant temperature with statement 1 mks b) at constant pressure with statement 1 mks c)	
	D		Determination of solubility and solubility product of sparingly soluble salt : For a sparingly soluble salt, the solubility and hence the conductance offered by the salt solution will be low, and the contribution by the saturated solution of a salt and that of pure water towards conductance may be comparable. Hence conductance of pure salt is obtained by taking difference between the conductance of the saturated solution of salt and	5

that of the water. For the saturated solution of the salt, the concentration term is replaced by solubility and molar conductance by limiting molar conductance of the salt.
Procedure :i) Measure the conductance offered by water (L_{water}) ii) prepare saturated solution of the sparingly soluble salt and then Measure the conductance offered by salt solution ($L_{salt\ sol.}$)
iii) measure the conductance offered by 0.1 N KCl solution (L_{kcl})
Calculations :
Determination of cell constant
k = Sp.cond. of 0.1 N KCl solution/ Conductance of 0.1 N KClsolutionnt.
Conductance of salt (L_{salt}) = $L_{salt\ sol}$ - L_{water}
Specific conductance of salt K_{salt} = L_{salt} x k (cell constant)

$\Lambda_c = \Lambda^0_{salt} = \Lambda^0_+ + \Lambda^0_-$

Solubility S = 1000 x K_{salt} / Λ^0_{salt} moles dm^{-3}

Solubility S x molecular weight of salt in terms of g dm^{-3}

Depending upon the formula of the salt , the solubility product of the salt can be calculated as follows
$K_{sp} = x^x y^y S^{x+y}$

E

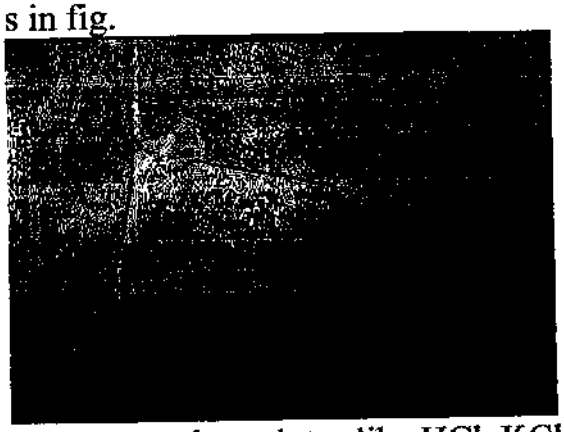
limiting molar conductance
The molar conductivity at infinite dilution or approximately zero concentration is considered as limiting molar conductance

<u>Strong electrolytes</u> : The molar or equivalent conductance of strong electrolyte increases with decreases of the concentration of electrolyte. This increase in conductance is linear with dilution at it reaches a maximum value or limiting value for the strong electrolyte. It is referred as limiting molar conductance .
Debye HuckelOnsager developed a mathematical expression to relate molar/ eq. conductance at zero concentration or at infinite dilution
$\Lambda_m = \Lambda_m^\circ - b$

Λ_m= Molar conductance at given dilution

11

Λ_m^o= Molar conductance at infinite dilution
B = constant which depends on the nature of solvent and dielectric constant of the solvent., C = concentration of solution.
A plot of Λ_m against shows that molar conductance is higher for dilute solutions and for the lower concentration. This is because for strong electrolyte the number of ions in the solution do not increase because they are almost completely ionized in the solution at all the concentrations. A plot of Λ_m against is s in fig.



For strong electrolytes like HCl, KCl, NaCl it is possible to determine Λ_m^oMolar conductance at infinite dilution from the plot of ofΛ_m against which is linear and extrapolation to Y axis gives the Λ_m^o i.e. limiting molar conductance for the strong electrolyte.

Weak electrolytes: A plot ofΛ_m against shows that in a concentrated solutions the molar conductance values are low and it increases steadily with dilution . Hence Λ_m^oMolar conductance at infinite dilution cannot be obtained by extra polation method

F

C = 0.1 mol dm^3, V = 7.2 cm^3, cross sectional area (a)= 0.112 cm^3, I = 65 x 10^{-4} amp,
t = 2400 sec, t_{K^+} = ?
.....1mks

Correct substitution 1 mks

13

			Rest of the calculation 3	
Q.3	A		Definition- 1 mark each(1x3), Explanation(any one)- 2 marks	5
	B		Neatly labelled correct MO diagram -3 marks Bond order formula with calculation -1 mark Correct magnetic property - 1 mark	5
	C		Representation of ground state & excited state w.r.t. outer configuration -2 marks Correct type of hybridisation -1 mark Correct geometry - 1 mark Structure -1 mark	5
	D		Stepwise representation of Born- Haber cycle with example Each step- 1 mark	5
	E		Explanation of formation of bonding and antibonding molecular orbitals – 2 marks each Suitable diagram – ½ mark each	5
	F		Correct formula -1 mark Substituiton of values appropriately -1 mark Correct answer -3 marksAns: -306kJ/mol	5
Q.4	A		Explanation with example -2 marks. Mechanism -3marks.	5
	B		Reaction for preparation of phenol -1mark. Explanation for phenol is a weak acid-2marks. What happens when phenol treated with –correct reaction -1 mark each.	5
	C		Explanation about organometallic compounds-2 marks Preparation -1mark each. Explanation for preparation of above organometallic under anhydrous condition-1 mark.	5
	D		Correct reaction products -1 mark each.	5
	E		Definition -1 mark. Classification with examples-2marks.	5

15

			Correct reaction for preparation-1 mark each.	
	F		Correct reaction -1 mark each.	5
Q.5				
	A		**Derive Van't Hoffs reaction isotherm.** Consider a reversible chemical reaction which takes place at constant temperature and pressure is of the type $aA + bB \leftrightarrows cC + dD$ then, the free energy associated with reactants and products can be given in terms of chemical potentials as- and The change in free energy associated with the chemical reaction can be given as .....① The chemical potential of a substance is given by the relation- Where a- activity of the substance, μ is chemical potential and μ^0 is standard chemical potential. Therefore, the chemical potential of constituents involve in the given reaction can be written as- On rearranging the above equation, it becomes- or The above equation is known as Van't Hoff reaction isotherm	
	B		cell constant of a conductivity cell : A cell constant of a conductivity cell is the ratio of the distance between two electrodes (l) to the area of cross- section (a) i.e. cell constant k = length l / area a the unit of a cell constant is cm^{-1}, m^{-1} (SI) Determination of cell constant of a conductivity cell : The cell constant of a conductivity cell could not be determined directly as it is quite difficult to measure the distance between two parallel electrodes and area of cross section of the	

17

			electrodes. Hence indirect method is employed to determine the cell constant of the cell. Procedure: prepare a 0.1 N KCl solution in conductivity water. Measure the conductance of 0.1 N KCl solution using conductivity cell for which a cell constant is to be determined. Specific conductance of 0.1 N KClsolution at the experimental temperature should be obtained from the literature /data. Then Cell constant can be calculated using equation Cell Constant = Specific conductance of 0.1 N KCl solution Observed conductance of 0.1 N KClsolution. The unit of cell constant is cm^{-1}.	
	C		Three corrections/ improvements with brief explanation -3 marks Improved Bond energy values -2 marks	5
	D		Neatly labelled molecular orbital diagram -2 marks Bond order calculation -1 mark Explanation -2 marks	5
	E		Explanation with kinetic and mechanism-3 marks. Energy profile diagram and comment on stereochemistry -1 mark each.	5
	F		Correct reaction -1 mark each	5