Q. P. Code : 30159

[Time : 03 Hours] **[Marks : 100]**

NB: 1. All questions are compulsory.

2. Figures to the right indicate full marks.

3. The use of non-programmable calculator/log-table is allowed.

Q.1 A] Select the correct option and complete the following sentences: 12

i) Fugacity has the same dimensions as_____.
(a) Pressure (b) temperature (c) volume

ii) The variation of _____with temperature is given by van't Hoff's reaction isochore.
(a) Free energy (b) entropy (c) equilibrium constant

iii) The equivalent conductance of a solution of an electrolyte _____with increase in dilution.
(a) decreases (b) increases (c) does not change

iv) In electrolytic conductors, ---------- act as carriers of electricity.
(a) ions (b) electrons (c) positrons

v) For non bonding orbitals integral overlap S _____
(a) equal to zero (b) > 0 (c) <0

vi) A triple bond contains_____ number of pi bonds
(a) one (b) two (c) three

vii) In SF_6 molecule, the atom S undergoes _____ hybridisation.
(a) sp^3d (b) sp^3d (c) sp^2

viii) The energy released in the formation of one mole of ionic solid from its constituent gaseous ions is known as _____
(a) exchange energy (b) ionisation energy (c) lattice energy

ix) Allyl aryl ethers on heating at about 200˚C undergoes rearrangement reaction which is known as _____
(a) Claisen Rearrangement (b) Fries Rearrangement (c) Kolbe Reaction

x) Alcohols on treatment with HI in presence of red phosphorus gives____
(a) Alkane (b) alkyl halide (c) alkyne

xi) Epoxidation of alkenes is done by using _____
(a) $KMnO_4$ (b) HNO_3 (c) peroxy acid

xii) Action of sodamide in liquid ammonia on p-bromo toluene gives _____
(a) only p-amino toluene (b) only m-amino toluene (c) mixture of p- toluene and m-amino toluene.

B] State whether the following statements are True of False 03

i) The transport number of an ion decreases with an increase in temperature.

ii) Born Haber Cycle helps to determine lattice energies of ionic compounds experimentally.

iii) The elimination-addition mechanism involves Benzyne intermediate formation.

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C] Match the following 05

Column A	Column B
1) For non-spontaneous process	a) $\Delta G > 0$
2) S.I. unit of cell constant	b) $\Delta G = 0$
3) Ionic bond	c) cm^{-1}
4) Oxygen molecule	d) non directional bond
5) *o*-nitrophenol	e) m^{-1}
	f) double bond
	g) Intra molecular hydrogen bonding
	h) Inter molecular hydrogen bonding

Q.2

A]i) Derive Gibb's –Helmholtz equation. 05

ii) Calculate the free energy change of a process whose enthalpy change at 373 K is -270.93×10^3 J and temperature coefficient of the process is 21.58 J. 03

OR

A]i) The equilibrium constant for a gaseous reaction is 169 at 500 K and its heat of reaction is -42.68×10^3 J. Calculate the equilibrium constant of the same reaction at 690 K. (Given R = 8.314 JK^{-1} mol^{-1}) 05

ii) Write a short note on " Partial molal properties". 03

B]i) Discuss the factors which affect transference number of an ion. 05

ii) At 291 K, the equivalent conductance at infinite dilution of NH_4Cl, NaOH, NaCl are129.8 S cm^2, 217.4 S cm^2 and 108.9 S cm^2 respectively. Calculate equivalent conductance at infinite dilution of NH_4OH. 03

OR

B]i) The transport number of H^+ ion is 0.847 in 0.005 M HCl solution. The cross-sectional area of the tube is 1.5 cm^2. Find the quantity of electricity required to displace the boundary through 1.4 cm. (F = 96485 C/mole). 05

ii) State and explain Kohlrausch's law of independent migration of ions. 03

C] Show that decrease in Gibbs free energy at constant pressure and temperature gives net work 04

OR

C]i) Define 04

i) Cell constant of conductivity cell

ii) Conductivity of electrolyte

iii) Transference number of an ion

iv) Equivalent conductance of an electrolyte at infinite dilution

Q3 A]i) What is limiting radius ratio of cation? How does it help in predicting its coordination number? 05

ii) Discuss in brief the crystal structure of CsCl. 03

OR

A]i) Write a Kapustinskii's equation and explain the terms involved in it. Using Kapustinskii's equation calculate the lattice energy of $CaCO_3$.The radius of Ca^{+2} is 114 pm. Radius of CO_3^{-2} is 185 pm. (Constant C = $1{\cdot}079 \times 10^5$.) 05

ii) What are the conditions to be satisfied by atomic orbitals to form molecular orbitals ? 03

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B]i) Discuss the importance of exchange energy and shielding effect in determining the bond energy and bond length in the formation of hydrogen molecule on the basis of valence bond approach. 05

ii) On the basis of hybridization, explain the geometry of BF_3 molecule. 03

OR

B]i) Write a brief note on the concept of resonance and resonance energy with suitable examples. 05

ii) Write a note on sigma and pi covalent bonds. 03

C] What is hybridisation? Explain sp^3d hybridisation with a suitable example. 04

OR

C] Write a brief note on gerade and ungerade orbitals . Give examples. 04

Q.4 A]i) Explain the mechanism of alkaline hydrolysis of tert-butyl bromide and give its energy profile diagram. 05

ii) Write the reaction between ethylene oxide and -

a) ammonia b) water c) HCN 03

OR

A]i) What are organometallic compounds? Write down the reaction between n-butyl lithium and – 05

a) CO_2 b) HCHO c) H_2O/H^+

ii) Write the reactions for the action of acidified $K_2Cr_2O_7$ on primary, secondary & tertiary alcohols. 03

B]i) Give preparation of ethylene oxide from:

a) Ethene b) vicinal halohydrin. 05

ii) Distinguish between S_N1 and S_N2 reactions. 03

OR

B]i) What are primary, secondary & tertiary alcohols? How they are synthesized? Explain with suitable example. 05

ii) How are α – and β – naphthols prepared using naphthalene sulphonic acids? 03

C] What is esterification and etherification of alcohols? Give one example of each. 04

OR

C]i) How is phenol prepared from cumene? 02

ii) How you will prepare the following compounds using Grignards reagent?

a) Carboxylic acid b) Ketone 02

Q.5 Attempt any four of the following—

a) Derive Gibbs-Duhem equation. 05

b) Explain the variation of equivalent conductivity with dilution for (i) weak electrolyte (ii) strong electrolyte. 05

c) On the basis of molecular orbital theory, explain the bonding and magnetic behavior of B_2 molecule. 05

d) With the help of diagrams explain the formation of bonding and anti-bonding molecular orbitals on the basis of wave mechanical treatment. 05

e) What is cine substitution? Explain with mechanism. 05

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f) What happens when:- 05

1) Ethylene oxide reacts with methanol in presence of H_2SO_4
2) Phenol is treated with Benzoyl Chloride.
3) Phenyl lithium reacts with methyl cyanide.
4) Sodium phenoxide reacts with methyl iodide
5) Phenol is treated with bromine water

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