

[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)

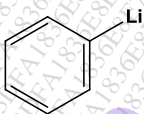
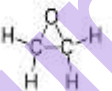
12

- (i) The change of free energy with pressure at constant temperature is related to _____
(a) volume (b) entropy (c) equilibrium constant
- (ii) Gibbs free energy is _____ property.
(a) Constitutive (b) extensive property (c) intensive property
- (iii) When reaction is carried out from aqueous solution K_{eq} is designated as _____.
(a) K_p (b) K_c (c) K_f
- (iv) On passing electrical current through an electrolyte solution _____.
(a) Anions moves towards cathode (b) cations moves towards cathode (c) both the ions moves towards cathode.
- (v) The sum of the transport number of cations and anions of an electrolyte is _____.
(a) 1 (b) -1 (c) 0
- (vi) The equivalent conductance of a solution of an electrolyte _____.
(a) Decreases with dilution, (b) Increases with dilution, (c) Does not vary with dilution
- (vii) In NaCl ionic crystal, the co-ordination number of positive ion is _____ that of negative ion.
(a) Greater than (b) Less than (c) Same as
- (viii) Born- Lande equation is used to calculate _____.
(a) Lattice energy (b) Solvation energy (c) Electron affinity
- (ix) Bond order in C_2 molecule is _____.
(a) 2 (b) 1 (c) 0
- (x) PCl_5 molecule has _____ structure.
(a) Trigonal (b) Trigonal bipyramidal (c) Tetrahedral
- (xi) _____ is least stable among the following
(a) C_2 (b) N_2 (c) B_2
- (xii) O_2^+ ion has _____ antibonding electrons more than O_2 molecule.
(a) one (b) two (c) three
- (xiv) SN^2 Mechanism generally results in a product having _____.
(a) Retention of configuration (b) Inversion of Configuration (c) Racemic Mixture
- (xv) Phenyl magnesium bromide reacts with Carbon dioxide to form an adduct which on subsequent acidic hydrolysis forms _____.
(a) Benzoic acid (b) Benzyl alcohol (c) Benzaldehyde
- (xvi) Alcohols react with acetyl chloride to form _____.
(a) ethers (b) anhydride (c) esters

- (xvii) Butyl Lithium reacts with water to form_____
- (a)1- butanol (b)Butane (c)2-butanol
- (xviii) The method of heating chlorobenzene with NaOH under pressure to form phenol is called_____
- (a)Claisen Rearrangement (b)Dows Reaction (c)Kolbes Reaction

- (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) For pure substance, chemical potential is entropy per mole.
- (iii) High electron affinity of non metal favours the formation of an ionic bond.
- (iv) BF_3 molecule has tetrahedral geometry.
- (v) Para nitro phenol is less acidic than phenol.
- (vi) SN^{i} mechanism is a second order reaction.

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

| Column X | | Column Y | |
|----------|---|----------|---------------------------|
| (i) | Cell constant | (a) | Oxetane |
| (ii) | Escaping tendency | (b) | 1/a |
| (iii) | sp hybridization | (c) | Phenyl Lithium |
| (iv) | Bonding molecular orbital | (d) | Oxirane |
| (v) | IUPAC name of  | (e) | Linear geometry |
| (vi) |  | (f) | Fugacity |
| | | (g) | Lithium benzene |
| | | (h)) | positive overlap integral |

Q.2

Attempt **any four** of the following.

- (A) Explain variation of chemical potential with pressure and temperature. 05
- (B) The equilibrium constant for certain gaseous reaction is 1.21×10^{-4} at 1200 K and 4.08×10^{-4} at 1400 K. Calculate heat of reaction . 05
(Given $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)
- (C) Write note on : Partial molal properties 05
- (D) Discuss the determination of ionic product of water by conductometric method. 05
- (E) The conductivity of 0.01 N acetic acid solution when measured in a conductivity cell of cell constant 1.05 cm^{-1} is found to be $4.32 \times 10^{-4} \text{ S}$, Calculate the degree of dissociation and dissociation constant of acetic acid at this concentration. 05
(Given $\lambda^\infty_{\text{CH}_3\text{COOH}} = 390 \text{ S cm}^2 \text{ g.eq}^{-1}$.)
- (F) Differentiate between electronic conductors and electrolytic conductors 05

Q.3

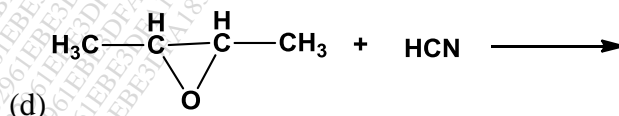
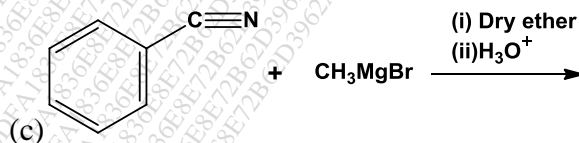
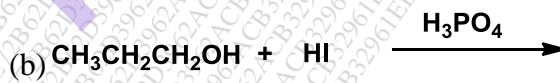
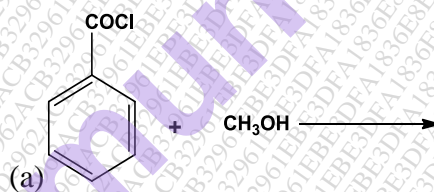
Attempt **any four** of the following.

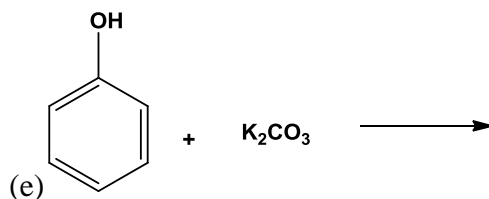
- (A) Define the term 'Resonance'. Give the different conditions for resonance. 05
- (B) State the different energies involved in stepwise determination of lattice energy by Born-Haber cycle and explain any two of them. 05
- (C) Show that the presence of lone pair of electrons affects the regular geometry of ammonia and water molecule.. 05
- (D) On the basis of LCAO method, explain the formation of bonding and antibonding molecular orbitals. 05
- (E) Draw the structures of SiCl_4 and XeF_4 molecules. State the type of hybridisation and geometries observed in them. 05
- (F) Define Radius ratio and limiting radius ratio. Calculate radius ratio and predict coordination number of Zn^{2+} in ZnSe ionic crystal. 05
- Radius of $\text{Zn}^{2+} = 0.74 \text{ \AA}$ Radius of $\text{Se}^{2-} = 1.98 \text{ \AA}$

Q.4

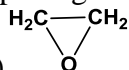
Attempt **any four** of the following.

- (A) Give the synthesis of α and β Naphthols. Which isomer is more stable α or β and why? What will be the product formed when β Naphthol is treated with Dimethyl Sulphate in presence of NaOH ? Give the reaction 05
- (B) What is Cine Substitution? Write a descriptive note on Cine Substitution. What will be the products formed when
(i) ortho bromo toluene
(ii) meta bromo toluene
(iii) para bromo toluene
are treated with NaNH_2 in liquour NH_3 05
- (C) Complete the following reactions : 05





- (D) How is propyl lithium prepared? Give any one method of preparation. 05
What is the action of the following reagents on propyl lithium?
explain giving reactions only :-



- (a) (b)HCHO (c)C₂H₅I
(E) How will you synthesize the following, give reactions only :- 05
(a)Dibutyl ether from butanol
(b)Ethylene chlorohydrin from ethylene oxide
(c)2,4,6- tribromo phenol from phenol
(d)Propylene oxide from propene
(e)Methyl Acetate from methanol
(F) Give any one method of preparation of ethanol ? Why does ethanol 05
have a higher boiling point than diethyl ether , even though their
molecular weights are the same?
What is the reaction of the following reagents on ethanol :-
(a) K₂Cr₂O₇ / H₂SO₄
(b)PCl₅

Q.5

- Attempt **any four** of the following. 05
(A) Derive van't Hoff's reaction isochore. 05
(B) Describe moving boundary method to determination of transport 05
number of ion.
(C) Draw molecular orbital diagram of H₂ and Li₂ molecule. Calculate 05
their bond order and mention magnetic property of each.
(D) Comment on shape of iodine pentafluoride molecule on the basis of 05
covalent bonding.
(E) Explain the mechanism of alkaline hydrolysis of tertiary butyl 05
bromide giving the energy profile diagram and stereochemistry of the
products formed..
(F) How will you convert the following, giving reactions only :- 05
(a)Ethylene oxide to ethanol amine
(b)Benzene sulphonic acid to phenol
(c)Methyl magnesium bromide to tertiary butanol
(d)2- propanol to propene
(e)Ethyl lithium to ethane

xxxxxxx