# 1 semester M.Sc Degree Examination, Jan/Feb-2021

### CHEMISTRY

## Inorganic Chemistry-I

# Time: 3Hr

#### Max.Marks: 80

 $(2 \times 8 = 16)$ 

Instruction: Answer any eight questions from part-I and any four full questions from part-II

## PART-I

- i) Electro negativity of nitrogen is higher than oxygen. Give reason.
- ii) How are Sigma ( $\sigma$ ) and Pai ( $\pi$ ) MO formed?
- iii) Why acetic acid is week acid in H<sub>2</sub>O and strong acid in Liq.NH<sub>3</sub>?
- iv) Is N<sub>2</sub> molecule is stronger than O<sub>2</sub> molecule? Justify the answer
- v) How Bonding and antibonding molecular orbitals are formed?
- vi) How are  $\sigma$  and  $\pi$  molecular orbitals formed?
- vii) Strong oxidizing agents do not apparently exist in liquid NH<sub>3</sub>, give reason.
- viii) What is radius ratio? Mention its significance.
- ix) Write any two chemical reactions carried out in liquid SO<sub>2</sub> as solvent?
- x) State the Bronsted-Lowry concept of acid and base. Give an example for each.

### PART-II

1. a) What are resonance hybrids? Illustrate the stability of carbonate and nitrate ions?

- b) Draw the MO diagram of F<sub>2</sub> molecular and account for its bond strength and magnetic property.
- c) Explain the factor affecting the ionic size. The inter nuclear distance of KCl is 286pm calculate the ionic radii of K<sup>+</sup> and Cl<sup>-</sup>.

#### (4+6+6=16)

- 2. d) Illustrate formation of a mole of BaO using Born-Haber cycle.
  - e) Explain the salient features of hydridization theory. Based on this predict the geometry of BF<sub>3</sub> and SiH<sub>4</sub>
  - f) What are electron deficient compounds? Explain the structure of diborane.

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- 3. g) Discuss the ionic character in covalent compounds.
  - h) What is Ionic bond? Discuss the various factors that favour the formation of ionic compounds.

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### CH: 1.1

i) Write short notes on n-type and p-type semiconductors.

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- 4. j) Discuss the types of chemical reactions carried out in Liquid ammonia?
  - k) Discuss the relationship between polarity of a solvent and its solvating power with different substances
  - How do you differentiate between o-hydroxy phenol and p-hydroxy phenol using IR and NMR?

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- 5. m) Give the Lives' concept of acids and bases. Outline its salient features.
  - n) Set up MO energy level diagram for CO and NO molecules and comment on their stability and magnetic properties.
  - o) The first ionization potential of nitrogen atom is higher than oxygen, similarly Electron affinity of Fluorine exothermic whereas nitrogen is endothermic. Give reasons.

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- 6. p) What are stoichometric and non-stoichometric defects in solids.
  - q) Discuss the general properties of ionizing solvents
  - r) Discuss the Lowry-Bornsted concept of acid and bases. How this concept is differ from Usanovich concept

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## CH: 1.2

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## CHEMISTRY

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Instruction: Answer any eight questions from part-I and any four full questions from part-II

## **PART-I** (2 x 8 = 16)

- i) Draw any three structural isomers possible of molecular formula  $C_3H_8O$ .
- ii) Define the terms conformation and configuration.
- iii) Which one most stable? Give reasion



- iv) What is recemic mixture? Discuss its optical activity.
- v) Among two which one is aromatic? Give reason



- vi) Discuss the classification of carbocations and their respective stability.
- vii) How do you prove the formation of carbeen intermediate in reaction?
- viii) Why benzene is not easily undergoing neucleophilc substitution reaction?
- ix) Aryne triple bond is more reactive than normal triple bond. Give reason.
- x) Discuss the influence of polarity of a solvent on  $S_N1$  and  $S_N2$  reaction?

## PART-II

- a) Discuss the potential energy diagram and stability of conformations of n-butane.
   b) What are geometrical isomers? Explain any one method of determining them.
  - c) With suitable example explain plane of symmetry and centre of symmetry.

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2. d) Write a note on Huckel rule and aromaticity.

e) With example, explain aromaticity and antiaromaticity on the basis of molecular orbital sdescription.

f) Write notes on catenanes and cryptands? Mention their uses.

### (4 + 6 + 6 = 16)

- 3. g) How do you obtain benzyne from bromo benzene? Explain the mechanism
  - h) Illustrate the sulfonation and desulfonation reactions of benzene.

i) Discuss the regeoselectivity observed in the electrophilic substitution reactions of alkenes.

$$(4+6+6=16)$$

- 4. j). What is  $S_N$  reaction? Illustrate the mechanism involved in this reaction
  - k) Briefly discuss the stereochemical output of  $S_N 1$  and  $S_N 2$  reactions with suitable examples
  - l) How do you recognize the electrophilic substitution reaction follows  $S_E1$  or  $S_E2$  mechanism?

$$(4+6+6=16)$$

- 5. m) What are selective reactions? Give examples. How they differ from stereospecific reactions?
  - n) Explain the aromaticity of [12]-annulenes and [14]-annulenes
  - o) Discuss the optical activities ob biphenols

#### (4+6+6=16)

- 6. p) Write a note on generation, identification and reactions of nitrenes intermediates?q) What are Markovnikoff's and anti- Markovnikoff's rules? Illustrate with example.
  - r) Discuss in brief neighbouring group participation in neucelophilc substitution reaction.

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### CHEMISTRY

### Physical chemistry-I

Time: 3Hr

Max.Marks: 80

 $(2 \times 8 = 16)$ 

Instruction: Answer any eight questions from part-I and any four full questions from part-II

### PART-I

- i) How Rayleigh-Jeans formula differ from Wien's Law?
- ii) What is photoelectronic effect?
- iii) Calculate the wavelength of an electron (m =  $9.109 \times 10^{-31}$ kg) having energy equal to 150 ev.
- iv) How order and rate of a chemical reaction relate each other?
- v) What is luminescence?
- vi) What is isobaric and isochoric process?
- vii) Distinguish between primary and secondary salt effects.
- viii) The rate constant for zero order reaction is 4  $X10^{-3}$  mol lit<sup>-1</sup> min<sup>-1</sup>. Calculate the t<sub>1/2</sub> of the reaction.
- ix) What is absolute entropy?
- x) Define the term oscillator strength.

### PART-II

- 1. a) The position of the electron (m= 9.19 x  $10^{-31}$  kg) in H-atom could be determined with an accuracy of 0.01nm. What would be the uncertainty in its velocity? (h = 6.6 x  $10^{-34}$  js)
  - b) Explain Hermitian and angular momentum operator.
  - c) Find the Egien value and Eigen function of a linear momentum operator.

(6+6+4=16)

- d) 50% of a first order reaction is completed in 23 min. Calculate the time required to complete 90% of the reaction.
  - e) Derive the rate expression for parallel reaction.
  - f) Discuss the effect of dielectric constant of the medium on rate of a reaction using single and double sphere models.

(6 + 6 + 4 = 16)

- 3. g) Show that the entropy is measure of unavailable energy and disorder of a system.
  - h) What does Gibbs free energy significance? How does it vary with temperature and pressure?
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i) Discuss briefly the Nearst heat thermo.

$$(6+6+4=16)$$

- 4. j) In the photochemical reaction A  $\rightarrow$  B, 1.5 X 10<sup>-3</sup> moles of B is formed as a result of the absorption of 4.0 X 10<sup>6</sup> ergs at 3000 Å. Calculate the quantum yield
  - k) Derive the rate expression fot the photochemical combination of hydrogen and chlorine.
  - Write notes on A) Quenching of fluorescence, B) Chemiluminescence and C) Sensitized chemiluminescence.

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- 5. m) Write the physical significance of wave function  $(\psi)$ 
  - n) Discuss the theoretical basis for the determination of fugacity of real gases by graphical method,
  - o) Derive the rate expression for reversible reaction.

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6. p) Deduce Gibbs-Duhem equation.

q) Explain the experimental determination of order with respect to a particular reactant and total order of reaction with an example.

r) Discuss the collision theory of bimolecular reaction.

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## CH: 1.4

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## CHEMISTRY

## Chemical spectroscopy

#### Max.Marks: 80

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Instruction: Answer any eight questions from part-I and any four full questions from part-II

## PART-I

- i) Distinguish between polarization and scattering.
- ii) Explain the fact that  $H_2$  and  $CH_4$  does not give rise to rotation spectra while HCl and  $CH_3Cl$  do.
- iii) Write the physical meaning of rigid and non rigid rotator.
- iv) State and explain Frank-Condon principle.
- v) Why  $CO_2$  has two absorption peaks in its IR spectrum?
- vi) Calculate the number of normal modes of vibrations of toluene.
- vii) Differentiate between stokes and anti-stokes lines in Raman spectra.
- viii) Define Quadrupole coupling constant.
- ix) What is chemical shift in NMR? Explain.
- x) What is zero field splitting?

## PART-II

1. a) Give the various regions of electromagnetic spectrum with their wave length and energy. Indicate the corresponding spectral techniques.

b) Deduce the structure of the chemical species which is obtained by the alkali metal reduction of benzene at  $-70^{\circ}$ C and exhibit seven lines in its ESR spectrum. Account for its spectral behaviour.

c) Write an explanatory notes on Spin-Orbit coupling and selection rules in ESR spectroscopy.

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- 2. d) Discuss the effect of isotopic substitution on rotation spectra of linear diatomic molecule.
  - e) Discuss the rotation spectra of diatomic molecules from the following points

i) Region of occurrence

- ii) Criteria for absorption and
- iii) Selection rules.

# Time: 3Hr

f) Write briefly on the empirical rules for predicting  $\lambda$  of maximum adsorption for conjugated dienes.

(4+6+6=16)

- 3. g) What do you understand by harmonic vibrations? Outline the general equation for vibrational energy of an anhormonic oscillator.
  - h) Discuss the vibration-rotation spectra of diatomic molecule.
  - i) Write a brief note on polarization of Raman lines and finger print region.

(4+6+6=16)

- 4. j) What is Spin-Spin coupling? How does it lead to multiplicity to the signals in NMR spectroscopy? Explain.
  - k) Discuss the theory underlying the NMR spectroscopy.

1) Explain the terms ionization process, molecular ion peak and base peak in mass spectroscopy.

$$(4+6+6=16)$$

- 5. m) Explain the rules for interpreting ESR spectra.
  - n) Discuss the various types of electronic transitions observed in organic molecules.

o) Write an explanatory notes on Karmer's degeneracy and selection rules in microwave spectroscopy.

### (4 + 6 + 6 = 16)

- 6. p) Depict the normal modes of a non-linear XY2 type molecule and explain their IR activity.
  - q) Illustrate how IR spectroscopy can be used to study the
    - i) Hydrogen bonding
    - ii) Ring strain and
    - iii) Mesomeric effect.

r) Give a brief account of relaxation process in NMR and factor affecting the chemical shift.

$$(4+6+6=16)$$