

III semester M.Sc Degree Examination, September/October-2020

CHEMISTRY

Inorganic Chemistry-III

Time: 3Hr

Max.Marks: 80

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

**PART-I**

(8 X 2 = 16)

- i) What are kinetically labile and inert complexes? Give an example for each.
- ii) Distinguish between intimate and stoichiometric reaction mechanism of coordination compounds
- iii) Square planar complexes always follow  $S_N2$  reaction mechanism give reason.
- iv) Illustrate the hapticity of organometallic compounds with suitable example.
- v) What are Fischer and Schrock alkylidene complexes? Give an example each
- vi) What are interhalogen compounds? Give two examples.
- vii) What are fluxional molecules? Give examples
- viii) Why Fisher carbenes are generally less reactive than Schrock carbenes?
- ix) What are one dimension conductors? Explain their uses.
- x) List the dissimilarity between halogens and pseudohalogens.

**PART-II**

1. a) Discuss the experimental evidences which support dissociative mechanism.  
b) Explain the factors affecting the rates of substitution reactions in square planar complexes.  
c) Explain  $S_N1CB$  mechanism of co-ordination compounds and account for its evidences.  
(4 + 6 + 6 = 16)
2. d) What is 18 electron rule? Explain its significance and stability.  
e) Explain the structure of organomagnesium compounds and discuss their reactions with aldehydes and nitriles organic compounds.  
f) What are alkylidyne complexes? Explain their structure and reactivity  
(6 + 6 + 4 = 16)
3. g) Discuss the structure and bonding in Gilman reagents and explain the reactions of Gilman reagents.  
h) What are carboranes? Discuss the different method of synthesis of carboranes and mention their applications

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i) Write brief notes on Ring-opening metathesis polymerization (ROMP) and Ring-closing metathesis (RCM).

**(6 + 6 + 4 = 16)**

4. j) What are the general properties associated with polysilanes? Explain different types of polysilanes and their preparation

k) What is trans effect? Explain the theories in support of trans effect.

l) Explain the method of Preparations of Interhalogen compounds and discuss the structures of interhalogen compounds

**(6 + 4 + 6 = 16)**

5. m) Explain the  $S_N1$  reaction mechanism and energy profile involved in octahedral complexes.

n) Discuss factors affecting the rates of substitution reactions in square planar complexes

o) Discuss the preparation of cis and trans  $[Pt(NH_3)(NO_2)Cl_2]$  from  $[PtCl_4]^{2-}$

**(6 + 4 + 6 = 16)**

6. p) What are borazines? Explain the different methods of synthesis of borazines.

q) What is Hydroformylation reaction? Explain the mechanism of this reaction using modified catalyst.

r) Discuss briefly about Wacker process and illustrate its mechanism, mention the advantages of copper salts.

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## CHEMISTRY

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## PART-I

(8 X 2 = 16)

- i) Write the equation for the number of vibrational degrees of freedom for linear and non-linear molecules.
- ii) Why methanol is a good solvent for UV but not for IR spectroscopy?
- iii) What is vicinal spin-spin coupling?
- iv) Write the pattern of  $^1\text{H}$  NMR spectra of ethylmethyl ether and specify the  $\delta$  values of protons on each carbon atom.
- v) What is long range coupling constant? Explain with suitable example.
- vi) What is sensitization? Explain its uses.
- vii) Why *trans* alkene is less stable *than* *cis* alkene under photochemical condition?
- viii) Explain the reason for extreme instability of three membered heterocyclic ring compounds?
- ix) Why furan is less aromatic than pyrrole?
- x) Explain the any one method of synthesis of pyrimidines.

## PART-II

1. a) Explain the Woodward-Fischer rules for calculating absorption maximum in  $\alpha$ ,  $\beta$  unsaturated carbonyl compounds.  
 b) How do you distinguish alcohol, acid and amide compounds in IR spectra.  
 c) Explain the salient feature of mass spectrum fragmentation of carbonyl compounds and alkylhalides.  
 (6 + 4+6 = 16)
2. d)  $\text{CH}_3$  proton in diemethylether appears at around  $\delta = 3.8-4.0$  where as in acetone they appears at  $\delta = 2.3-2.5$  in  $^1\text{H}$ -NMR spectra. Explain the reason.  
 e) What is spin decoupling? Explain its advantages in  $^{13}\text{C}$ -NMR spectrum.  
 f) Explain the theory of 2D NMR.  
 (6 + 6 + 4 = 16)

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3. g) Name and write the different isomers of benzene molecule formed under photochemical condition.

h) Discuss Norrish type I and Norrish type II cleavage with suitable examples.

i) What is singlet oxygen molecule? How would you generate them? Explain the various reactions involved in singlet molecular oxygen?

**(4 + 6 + 6 = 16)**

5. j) Explain any two methods of synthesis of furan and pyrrole.

k) Explain the Fischer indole synthesis and write its mechanism.

l) Discuss the aromaticity and pyridine? Compare the basicity of pyridine and piperidine.

**(6 + 4 + 6 = 16)**

6. m) Write a note on absorption and Intensity shifts.

n) What is Retro-Diel's-Alder reaction?

o) Discuss spin-lattice relaxation (longitudinal relaxation)  $T^1$  and explain its significance.

**(6 + 4 + 6 = 16)**

7. p) Write the different isomers of triazines and comment their stability.

q) Write a note on photochemical reactions involved in green house effect.

r) Draw the Jablonski diagram and define the terms phosphorescence and fluorescence.

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CHEMISTRY

Physical Chemistry-III

Time: 3Hr

Max.Marks: 80

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

**PART-I**

(8 X 2 = 16)

- a) Distinguish between specific and general acid-base catalyzed reaction.
- b) What is acidity function? Give its significance
- c) How dose catalysis enhance the rate of reaction?
- d) What are the causes of overvoltage?
- e) Explain the terms anodic current and cathodic current
- f) Why gelatin is added during the polarography experiment?.
- g) Define Van't Hoff factor. Give its significance.
- h) What are intrinsic semiconductors? Give an example.
- i) Differentiate between Bravais lattice and space lattice.
- j) What are isotonic solutions?

**PART-II**

1. a) Explain Hammelt's linear free energy relations and its significance.  
b) Discuss the explosion limits with reference to branched chain reactions  
c) Discuss the kinetics of the flow method for the study of fast reactions  

(4 + 6 + 6 = 16)
2. d) What is concentration over potential? Explain the experimental determination of over potential.  
e) Explain Tafel's theory for activation overovltage.  
f) Explain the measurement of diffusion current by dropping mercury electrode (DME) method and its quantitative applications.  

(6 + 6 + 4 = 16)
3. g) Distinguish between Schotty and Frankel defect.  
h) Discuss the type-II semiconductor with an example.

i) What are superconductors? Give example and discuss briefly about effect of magnetic field on superconductors?

**(5 + 5 + 6 = 16)**

4. j) If 67.7g of urea ( $C_2H_4N_2O$ ) is dissolved in 833g of chloroform, calculate the elevation in boiling point of chloroform, ( $K_b$  of chloroform is 4.68).

k) Discuss the theoretical aspects of determination of molecular weight of solute by ebullioscopic method.

l) Write notes on following i) theories of osmosis and ii) reverse Osmosis.

**(6 + 4 + 6 = 16)**

5. m) What is half-wave potential? Discuss its applications.

n) Explain the Tafel equation and its applications in understanding the reaction mechanism.

o) What is explosion? Discuss gas-phase auto oxidation reaction.

**(6 + 4 + 6 = 16)**

6. p) Derive the relation between Bragg angle and Miller indices for a tetragonal Crystal system.

q) Explain the mechanism of electrochemical corrosion by inhibitors method.

r) Discuss how Evans diagram helps in the determination of corrosion current and corrosion potential.

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CHEMISTRY

Bio-Inorganic and Bio-Physical Chemistry-III

Time: 3Hr

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

PART-I

(8 X 2 = 16)

- i) What are ionophores? Give example.
- ii) List the different proteins used for Iron storage in cell.
- iii) What are electron transfer process?
- iv) Write a various biological processes carried out by zinc enzymes.
- v) What is biological nitrogen fixation?
- vi) Write the plasma level-time curve and indicate the MIC and MTC in the figure.
- vii) What is salt in process?
- viii) Write the effect of temperature on enzyme catalyzed reaction.
- ix) Explain the effect of  $\text{Cr}^{3+}$  on oxidation of glucose by glucose oxidation.
- x) Differentiate between blood plasma and serum.

PART-II

1. a) Briefly explain the biochemistry of Sodium, Potassium and Chlorine.  
b) What are coupled transporters? Explain their role in ion transporting.  
c) Explain the Mechanism of blood clotting.  

(4 + 6 + 6 = 16)
2. d) Explain the structure and functions of Hemoglobin and Myoglobin  
e) What are cytochromes? Discuss the structure and function of cytochrome C.  
f) Write a short note on metal clusters present in dinitrogenase and explain their role.  

(6 + 6 + 4 = 16)
3. g) Derive the expression for effect of [substrate] on enzyme catalyzed reaction (Michalein-Menten equation).  
h) Discuss the kinetic and mechanistic application of glucose oxidase in the oxidation of glucose.  
i) Explain substrate inhibition of Enzyme catalyzed reaction at constant [E] (6 + 6 + 4 = 16)

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4. j) What is Donnan membrane equilibrium? Discuss the biological significance of Donnan membrane equilibrium.
- k) Discuss the process salting out of proteins and explain its application in separation of proteins.
- l) What is viscosity? Discuss the effect of temperature and pH on viscosity.
- (6 + 4 + 6 = 16)**
5. m) What is ion pump? Explain Sodium and Potassium pump and the selectivity of the process.
- n) What are passive carriers? Give example and explain how they transport ion.
- o) Explain the structure and iron storage method in Transferrin and Sidrophores (Bacterial iron transmit).
- (6 + 4 + 6 = 16)**
6. p) Discuss the diffusion of solution across biomembrane and mechanism of application in the respiratory exchange of O<sub>2</sub> and CO<sub>2</sub>.
- q) How intrastrand disulfide bonds in proteins can be determined using viscosity measurement?
- r) What is meant by Osmoregulation? Explain its biological applications.
- . (6 + 4 + 6 = 16)**