19MCHE H101 REG.NO.....

EX - 2

CREDIT- BASED FIRST SEMESTER M.Sc. DEGREE EXAMINATION, NOVEMBER 2019

M.Sc. CHEMISTRY

INORGANIC CHEMISTRY THEORY - I

Time: 3 Hrs Max. Marks: 70

UNIT –I

PART A

1 Answer any TEN of the following: **(2×10=20)**

a. Arrange the following ions: Sr^{2+}, Ba^{2+}, Ca^{2+}, Mg^{2+} in the order of increasing ironic ratio. Justify the answer.
b. Mention the Geometry and hybridisation in ClF_3.
c. Electron affinities of S & Cl are higher than O & F. Give reason.
d. Give Usanovich definition for acids and bases.
e. What are Lewis acids? Arrange the following in the order of increasing acid strength BCl_3, BI_3, BF_3
f. Identify the conjugate acid and base in the hydrolysis of Ammonia.
g. Differentiate between the terms accuracy and precision.
h. Write Von-Weimarn equation. Mention its significance.
i. What is redox indicator? Give an example.
j. At low temperature, carbon monoxide is a better reducing agent than carbon. Justify.
k. What are disproportionate reactions? Give an example.
l. What are Pourbaix diagrams?

PART B

Answer any Five questions selecting at least one question from each unit. **(10×5=50)**

UNIT –I

2. a. Derive Born Lande's Equation.
   b. Discuss the bond order in O_2^{2-} and O_2^- ions with energy level diagram.
   c. Why is the first ionisation energy of the transition elements reasonably constant? (4+3+3)

3. a. Derive Pauling's Equation of electronegatvity.
   b. Write the increasing order of solubility of LiCl, KCl and NaCl in water. Justify the answer based on lattice energy concept.
   c. Draw neat diagram for the unit cell of NaCl and CsCl and find out number of particles present in an unit call of each. (4+3+3)

UNIT –II

4. a. Differentiate between Arrhenius and Bronsted-Lowry concepts of acids and bases.
   b. Explain why Na_2O and P_2O_5 behave as Lux-Flood acid and base respectively in water.
   c. Explain why acetic acid and nitric acid behave as bases in sulphuric acid. (4+3+3)

5. a. Discus any two applications of Pearson's concept of HSAB.
   b. Discuss the neutralization and metathetical reactions of liquid SO_2. (4+6)

UNIT –III

6. a. Explain any three types of determinate errors.
   b. What is a titration curve? Discuss the neutralization of a strong acid verses strong base.
   c. What is metal ion indicator? Explain its working principle.

7. a. The amount of oxalic acid present in a given solution was determined by two methods, the standard and the other new, when the following results were obtained. Find the value of student's 't' test.

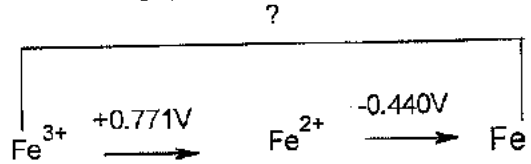
Sample number	Amount of oxalic acid determined by	
	Standard method	New method
1	8.33	9.12
2	11.24	10.65
3	7.98	8.23
4	13.36	12.32
5	16.98	17.98
6	11.34	12.12

   b. Define the terms: Supersaturation, Co-precipitation and Post-precipitation and explain how can these be avoided. (5+5)

UNIT –IV

8. a. Draw an Ellingham diagram for metal oxides and explain what information can be obtained from it.
   b. Construct Latimer diagram for the water, oxygen and hydrogen peroxide. SRP values for the stepwise conversion are +0.70V and +1.76V respectively. Convert it into Frost diagram.
   c. Explain any two properties of nanomaterials. (3+4+4)

9. a. Calculate skip potential for the following Latimer diagram?



   b. Give any two methods of synthesis of nanomaterials.
   c. Give any four applications of Frost diagrams. (3+4+4)

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19MCHE H102 REG.NO.....

CREDIT- BASED FIRST SEMESTER M.Sc. DEGREE EXAMINATION, NOVEMBER 2019

M.Sc. CHEMISTRY

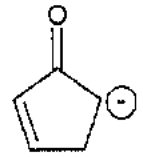
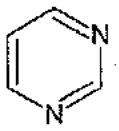
ORGANIC CHEMISTRY THEORY-I

Time: 3 Hrs Max. Marks: 70

PART A

1. Answer any TEN of the following: **(2X10=20)**

a) Classify the following compounds into aromatic, non-aromatic and anti-aromatic:

i) 
ii) 
iii) 
iv) [18]-Annulene

b) Write the resonance structure of

i) p-Nitrophenol ii) p-Methoxybenzoic acid

c) Write any two applications of Crown ethers.

d) How is benzyne obtained and trapped? Explain.

e) Predict the product in the following:

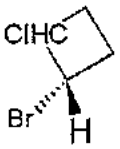
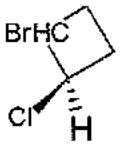
cis-2-butene+singlet carbene→ ?

trans-2-butene+singlet carbene→ ?

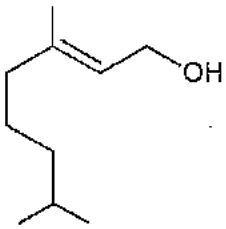
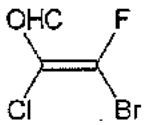
f) What is Kinetic isotope effect? Illustrate it with an example.

g) Write the Saw-horse and Newman projection formulae of meso-2,3 dihydroxy butane.

h) Assign R/S configuration of the following compounds:

i) 
ii) 

i) Designate E/Z – configuration for the following compounds:

i) 
ii) 

j) What is muta rotation? Give an example.

k) Give the structure of cellobiose and sucrose.

l) How do you achieve the following conversion.

D – Arabinose $\xrightarrow{?}$ D – Fructose

PART B

Answer any Five questions selecting at least one question from each unit. **(10X5=50)**

UNIT –I

2. a) Write a note on

   i) Charge transfer complexes
   ii) Hyperconjugation
   iii) Inclusion compounds

   b) Differentiate between the following :
   i) Intra and Intermolecular hydrogen bonding
   ii) Dipole – dipole and Dipole – Induced dipole interaction. (6+4)

3. a) Discuss the effect of resonance and inductive effect on acid and base strength of organic compounds with examples.
   b) Explain the aromaticity of non-benzenoid compounds with examples. (6+4)

UNIT –II

4. a) Illustrate with suitable examples for the following techniques in determining mechanism of reaction.
   i) Isotope labelling ii) Cross over experiments
   b) Explain the factors affecting the stability of carbanions. (6+4)

5. a) Write a note on
   i) Classical and non-classical carbocations ii) Nitrenes
   b) Discuss the two important kinetic methods of determining reaction mechanisms. (5+5)

UNIT –III

6. a) Explain optical activity in the following :
   i) Biphenyl and its derivatives ii) Spiranes
   b) Give a brief account of geometrical isomerism in oximes. (6+4)

7. a) Explain the Cram's and Prelog's rule
   b) Discuss the conformational analysis of substituted cyclohexane.
   c) Discuss any two methods of resolution of racemic mixtures. (3+3+4)

UNIT –IV

8. a) Explain the utility of the following techniques in the structural elucidation of polysaccharides.
   i) Periodate oxidation ii) Smith degradation
   b) Write a note on esters of carbohydrates and amino sugar. (6+4)

9. a) Give a brief account of configuration of glucose.
   b) Discuss the structure of chitin.
   c)How can be the structure of maltose established. (3+3+4)

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19MCHE H103 REG.NO.....

CREDIT- BASED FIRST SEMESTER M.Sc. DEGREE EXAMINATION, NOVEMBER 2019

M.Sc. CHEMISTRY

PHYSICAL CHEMISTRY THEORY -I

Time: 3 Hrs Max. Marks: 70

PART A

1. Answer any TEN of the following: **(2x10=20)**

a) Entropy is a measure of unavailable energy. Justify.
b) Describe the effect of change in concentration according to Le Chatelier's principle.
c) Deduce the meaning of Stirling's approximation.
d) The rotational constant of gaseous HCl, determined from microwave spectroscopy, is $10.59cm^{-1}$. Calculate the rotational partition function of HCl at 100K and 500K. ($B = 10.59cm^{-1}$ & $\sigma = 1$)
e) State Dulong & Petit law.
f) Differentiate between the terms force and fluxin irreversible thermodynamics.
g) Conventional methods cannot be employed to study fast reactions. Give reasons.
h) Calculate the activation energy of a reaction whose rate constant is tripled by a $20^{\circ}C$ rise in temperature in the vicinity of $27^{\circ}C$.
i) Write the Hammett equation and specify its limitations.
j) What are quantum mechanical operators? Give examples.
k) What are operators? Give an example.
l) Differentiate between Normalized and Orthogonal wave functions.

PART B

Answer any Five questions selecting at least one question from each unit. **(5×10=50)**

UNIT –I

2) a) Explain how the absolute entropy of a substance is determined with the help of law of thermodynamics.
b) Derive any two Maxwell's relation.
c) Explain the concepts of phase space, micro and macrostates. (4+3+3)

3) a) Derive the expression for Maxwell- Boltzmann statistics with the help of thermodynamic probability of a macrostate & Lagranje's undetermined multiplets.
b) Explain the concept and varities of ensembles.
c) What is meant by chemical potential? Derive the Gibbs-Duhem equation. (4+3+3)

UNIT –II

4) a) Explain briefly the Debye theory of heat capacities of solids.
b) Derive an expression for entropy production in chemical reactions.
c) How is the equilibrium constant calculated in terms of partition functions? Explain. (4+3+3)

5) a) Deduce the Sackur – Tetrode Equation.
   b) Evaluate the rotational partition function for a diatomic molecule.
   c) Explain the criteria for non- equilibrium states.

(4+3+3)

UNIT –III

6) a) Explain the following with the help of the Arrhenius equation
   i) The determination of the Energy of Activation.
   ii) The rate constant of a second-order reaction is 5.70×10^{-5} $dm^3 mol^{-1} s^{-1}$ at 25 °C and 1.64×10^{-4} dm^3 $mol^{-1} s^{-1}$ at 40 °C. Calculate the activation energy and the Arrhenius pre-exponential factor.
   b) Explain the Marcus theory of electron transfer.
   c) Describe any two methods for studying kinetics of fast reactions.

(4+3+3)

7) a) Illustrate the influence of ionic strength & the nature of the solvent on the rates of ionic reactions.
   b) Describe the Lindemann theory of unimolecular reactions.
   c) Explain the linear free energy relationship. (4+3+3)

UNIT –IV

8) a) State the set of approximations introduced by Huckel, for the linear conjugated systems.
   b) Describe the quantum mechanics of a simple harmonic oscillator.
   c) State the postulates of quantum mechanics. (4+3+3)

9) a) Derive Schrodinger's equation for a particle in one dimensional box.
   b) Explain the HMO theory of an allyl cation system.

(6+4)

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19 MCHE S104 REG.NO.....

CHOICE- BASED FIRST SEMESTER M.Sc. CHEMISTRY DEGREE EXAMINATION
NOVEMBER 2019

ANALYTICAL CHEMISTRY & MOLECULAR SPECTROSCOPY

Time: 3 Hrs Max. Marks: 70

PART A

I Answer any TEN of the following: **(2×10=20)**

a) Justify: -Using the same volume of solvent, the multi-step extraction is always better than the single step extraction.
b) What is meant by step grade adsorption column?
c) Differente between ascending and descending chromatographic methods.
d) List out the types of deviation observed in Beer's law? Give reasons for the same.
e) What are the disadvantages of flame atomisation procedure?
f) What are the criterion to decide whether turbidimetry or nephelometry should be used in the analysis of a medium containing suspended particles?
g) What is the maximum number of plates that can be obtained from any particle size in a given elution time?
h) Why gold coating is done prior to the scanning electron micrographs recording?
i) Why DSC technique is better to determine heat of a reaction than DTA?
j) The frequency of OH stretching vibration in CH_3OH is 3300cm^{-1}. Estimate the frequency of OD stretching vibration in CH_3OD.
k) Alternate lines of P and R branches of acetylene are less intense. Why?
l) The normal modes of vibration of CO_2 molecule are $\bar{\upsilon}_1$ = 1330 cm^{-1}, $\bar{\upsilon}_2$ = 667 cm^{-1}, $\bar{\upsilon}_3$ = 2349 cm^{-1}. Calculate the zero point energy of carbon dioxide molecule.

PART B

Answer any Five questions selecting at least one question from each unit. **(10×5=50)**

UNIT –I

2) a) In the distribution of a solute between water (C_1) and chloroform (C_2), the following results were obtained.
C_1 = 0.016 0.0237
C_2 = 0.338 0.753
What information we get regarding molecular state of the solute in chloroform?
b) Explain the procedure used for the preparation of sample for ICP technique?
c) In a reverse phase column, a solute was found to have a retention time of 31.3 min and an unretained species requires 0.48 min for elution when the mobile phase was 30% (by volume) methanol and 70% water. Calculate retention factor K and the composition of water-methanol composition that should bring K value of 5.
(Polarity index of methanol and water is 5.1 and 10.2 respectively) (4+3+3)

3) a) Write a note on thin layer chromatography.
b) How column efficiency, symmetry factor and capacity factor affect HPLC?.
c) Explain the types of detectors used in gas chromatography? (4+3+3)

UNIT –II

4) a) Explain the principle and procedure used to determine sulphate by turbidimetry?
   b) List out the fuels and oxidisers used in atomic absorption spectroscopy? What temperatures are attained in each case?
   c) How can you simultaneously determine two components in a solution using spectro photometry? (4+3+3)

5) a) Describe the procedure used for the preparation of sample for inductive coupled plasma emission spectroscopy.
   b) Write the merits and demerits of premix burners and total consumption burner.
   c) An absorbance of 0.436 was obtained after 11.5 cm^3 of titrating agent was added to 68cm^3 of an initial solution. What was the corrected absorbance of the solution. What would be the percentage error if the correction was made? (4+3+3)

UNIT –III

6) a) Explain the role of the following in thermal analyses taking suitable examples.
   a) sample size b) furnace c) particle size
   b) Draw and compare the DTA curves for the decomposition of calcium oxalate in the following atmospheres
   a) air b) CO_2 c) argon
   c) How can you study the morphology and the interplanar distances using transmission electron microscope? (4+3+3)

7) a) Describe the types of electron beam interactions which occur in microscopic techniques?
   b) Write the differences between compensated DSC and heat flux DSC?
   c) Explain the determination of isothermal crystallisation rates of high polymers using DTA. (4+3+3)

UNIT –IV

8) a) How centrifugal distortion constant helps to determine the force constant of a bond?
   b) The Raman lines associated with the vibrational mode which is both Raman and IR active is found at 4600A°, when excited by light of wavelength of 4358A°. Calculate the wavelength of the corresponding infrared band?
   c) Describe the characteristic features of rotational vibration spectra? (3+4+3)

9) a) Write a note on the inversion of ammonia molecule?
   b) By applying mutual exclusion rule, determine the structure of sulphur dioxide.
   c) The fundamental band of HCl is centered at 2886 cm^{-1}. Assuming that the internuclear distance is 1.276A°. Calculate the wave number of the first two lines of each of the P and R branches of HCl. (4+3+3)

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