ED-305

M.Sc. 1st Semester
Examination, March-April 2021

CHEMISTRY

Paper - I

Group Theory and Chemistry of
Metal Complexes

Time : Three Hours] [*Maximum Marks* : 80
[*Minimum Pass Marks* : 16

Note : Answer **all** questions. The figures in the right-hand margin indicate marks.

Unit-I

1. (*a*) Explain different types of plane of symmetry with example. 6

(*b*) Construct multiplication table of C_{3v} point group. 8

(*c*) Explain mutual exclusion principle with example. 6

OR

(*a*) Explain conjugacy relation and classes. 6

(*b*) The character table of D_3 point group is given below. By direct product method determine the product $E \times E$ and reduce it into the sum of irreducible representations. 8

D_3	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

(*c*) Evaluate the products σ_v, σ_y' and $C_2\sigma_v$ for a C_{2v} point group. 6

Unit-II

2. (*a*) Describe ligand group orbitals and symmetry matched metal atomic orbitals appropriate for σ bonding in an octahedral ML_6 complex. 5

(*b*) Explain uses of IR Spectra to determine structure of metal carbonyls. 10

(*c*) Explain nephelauxetic effect. 5

OR

(*a*) Using MOT explain why F^- is a weak ligand. 7

(*b*) Describe preparation, properties and structure of $Ni(CO)_4$. 7

(*c*) Write method of preparation and structure of dinitrogen complex. 6

Unit-III

3. (*a*) Describe spectrophotometric method for the determination of stability constant and composition of a complex. 7

(*b*) Explain structure of isopoly and heteropoly acids of W. 8

(*c*) Write a short note on silicides. 5

OR

(*a*) What is chelate effect ? Explain the factors affecting it. 7

(*b*) Describe classification of silicates with example. 7

(*c*) Write a short note on nitrides. 6

Unit-IV

4. (*a*) Explain structure of higher boranes. 8

(*b*) Explain structure of tetrameric phosphazenes. 6

(*c*) Write a short note on trinuclear, tetranuclear metal clusters. 6

OR

(*a*) Describe method of preparation and structure of carboranes. 7

(*b*) Explain chain catenation and heterocatenation. 7

(*c*) Explain structure of borazines. 6

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Paper - II

Concepts in Organic Chemistry

Time : Three Hours] [*Maximum Marks* : 80

Note : Answer **all** questions. The figures in the right-hand margin indicate marks.

Unit-I

1. (*a*) Which type of molecules exhibit delocalized bonding ? Discuss the molecular orbital picture to explain delocalized bonding and aromaticity of benzene. 5

(*b*) Explain the following :

(*i*) Aromaticity of 4π and 8π electron system 5

(*ii*) Conjugation and cross conjugation 5

(*iii*) Cyclopentadienyl cation is antiaromatic while cyclopropenyl cation is aromatic 5

OR

(*a*) Explain bonding in fullerenes. 6

(*b*) Heat of hydrogenation of cyclohexene is –28.6 k cal/mole. The observed heat of hydrogenation of benzene to cyclohexane is –49.8 k cal/mole. Find out the resonance energy of benzene. 4

(*c*) Explain aromaticity on the basis of Huckel rule. Explain the aromaticity of azulenes. 10

Unit-II

2. (*a*) Define conformation and configuration. Draw the various conformers of disubstituted cyclohexanes. Which conformer will be more stable and why ? 8

(*b*) Discuss optical activity of allenes and spiranes. 8

(*c*) Explain the term chiral and achiral with suitable examples. 4

OR

Explain the following terms : 5×4

(*a*) Optical purity

(*b*) Methods of resolution

(*c*) Hybridization of atoms

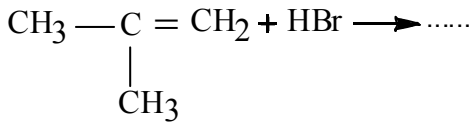
(*d*) Synthetic organic chemistry

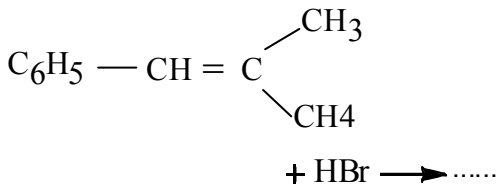
Unit-III

3. (*a*) Account for generation, structure, stability and chemical reactions of carbocations. 10

(*b*) Give the mechanism of Hunsdiecker reaction. 6

(*c*) Complete the following reactions and indicate reaction intermediate in each case – 4

(*i*) 

(*ii*) 

OR

(*a*) Explain E_1 and E_2 mechanisms. 10

(*b*) Describe the generation and reactivity of nitrene. 5

(*c*) Write a note on Saytzeff's rule. 5

Unit-IV

4. (*a*) Classify pericyclic reactions and explain correlation diagram taking example of 1, 3, 5 – hexatriene and 1, 3 – hexadiene system. 10

(*b*) Explain the following : 5×2

(*i*) Ene reaction

(*ii*) Cope rearrangement

OR

(*a*) Describe with suitable example of 3, 3 and 5, 5 – sigmatropic rearrangements. 10

(*b*) Explain the following : 5×2

(*i*) 1, 3 dipolar cycloaddition reaction

(*ii*) Woodward-Hoffmann selection rule.

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CHEMISTRY

Paper - IV

Theory and Application of Spectroscopy

Time : Three Hours] [*Maximum Marks* : 80

Note : Answer **all** questions. All parts of answer of each question should be written in one place. Be precise and to the point in your answer. The figures in the right-hand margin indicate marks.

Unit-I

1. (*a*) Explain which of the following molecules exhibit (*i*) pure vibrational and (*ii*) pure rotational spectrum : 4

H_2O, HCl, BF_3, CO_2, CH_4, CCl_4, C_6H_6, N_2, O_2

(*b*) Explain the following terms with reference to electromagnetic radiations : 8

(*i*) Scattering

(*ii*) Dispersion

(*iii*) Absorption and Emission

(*iv*) Polarization

(*c*) Describe uncertainty principle with its significance in spectroscopic techniques. 8

OR

(*a*) "Atomic spectrum is line spectrum whereas molecular spectrum is obtained as band." Give proper explanation. 4

(*b*) Explain the following : 8

(*i*) Natural line width

(*ii*) Intensity of spectral lines

(*c*) In which region of electromagnetic spectrum do the following frequencies exist ? 8

(*i*) 5 cm^{-1}

(*ii*) 1000 cm^{-1}

(*iii*) 12500 cm^{-1}

(*iv*) 60000 cm^{-1}

Explain the spectroscopic techniques associated with these spectrum.

Unit-II

2. (*a*) The rotational constant for H^1Cl^{35} is observed to be 10.5909 cm^{-1}. What are the values of B for H^1Cl^{37} and D^2Cl^{35} ? 4

(*b*) What is rotational constant ? Compare the energy levels of a rigid diatomic rotor with its isotopically substituted molecule and discuss the discrepancy. 8

(*c*) How microwave spectroscopy is useful in the determination of bond length ? Calculate the rotational constants of H_2 and HCl molecules. The bond lengths of H—H and H—Cl are 200 pm and 136 pm respectively. 8

OR

(*a*) How pure rotational spectrum is obtained ? Explain line spacing obtained in this spectrum. 4

(*b*) Classify molecules in terms of their moment of inertia and indicate which of the following molecules will show a microwave rotational spectrum : 8
H_2, CH_3Cl, CH_2Cl_2, O_3, SF_6, C_2H_2, NH_3, CH_3CHO

(*c*) Describe rotational spectra of linear polyatomic molecule. 8

Unit-III

3. (*a*) Write the basic principle of Auger spectroscopy. 4

(*b*) Write the principle and applications of electron diffraction microscopy. 8

(*c*) Explain variables on which intensities of Auger electron spectrum peaks depend. 8

OR

(*a*) Explain the process of phosphorescence describing it's applications. 4

(*b*) Describe theory, instrumentation and applications of fluorometry. 8

(*c*) Explain the terms 'optical density' and 'turbidity'. Describe the instrument that can be used for measurement of optical density. 8

Unit-IV

4. (*a*) Write down the Quantum theory of Raman effect. 4

(*b*) Describe Resonance Raman Spectroscopy 8

(*c*) Explain selection rules for pure-rotational, vibrational and vibrational-rotational Raman spectra. 8

OR

(*a*) Why it is often desirable to determine Raman spectra in the gas phase ? 4

(*b*) Write a note on CARS. 8

(*c*) Write instrumentation, advantages and limitations of Raman spectroscopy. 8

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Paper - III

Quantum Chemistry: Thermodynamics and Chemical Dynamics – I

[Time: Three Hours] [Maximum Marks: 80]

Note: Answer all questions. The numerals written in the right hand margin indicate marks.

Unit I

1. **(a)** Construct the potential energy operator of a particle subjected to a harmonic oscillator potential. **10**

   (b) Calculate the ground state energy for an electron that is confined to a potential well with a width of 0.4 nm. ($h = 6.626 \times 10^{-34}$ Js, $m = 9.109 \times 10^{-31}$ kg) **6**

   (c) Evaluate: **4**

$$\int_3^6 (2x^2+3x=5)dx$$

Or

(a) Apply Schrodinger wave equation to a particle in one dimensional box and obtain the expression for the Eigen function and Eigen values of the energy. **10**

(b) Solve the following: **4**

$$\frac{d}{dx}\left(\frac{e^x}{\sin x}\right)$$

(c) Find the value of **6**

$$\int \frac{dx}{(a-x)(b-x)}$$

Using the principle of partial fraction.

Unit II

2. **(a)** Differentiate between the terms activity and fugacity. Discuss any one method for the determination of fugacity. Explain effects of temperature and pressure on variation of fugacity. **10**

(b) Define partial molar free energy and derive Gibbs Duhem equation. **6**

(c) Discuss the chemical potential of ideal gases and pure solids. **4**

Or

(a) Define partial molar property. What is the physical significance of partial molar property? Discuss any one method for the determination of partial molar property. **10**

(b) Derive Van't Hoff equation representing the variation of equilibrium constant with temperature. **6**

(c) Verify the following Maxwell relations: **4**

(i) $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

(ii) $\left(\frac{\delta T}{\delta P}\right)_T = \left(\frac{\delta V}{\delta S}\right)_P$

Unit III

3. **(a)** Discuss thermodynamics of electrified interfaces and Lippmann's equation. **10**

(b) Compare the ionic strengths of solutions of uni-univalent, uni-bivalent and bi-bivalent electrolytes at the same molality, assuming complete ionization. **5**

(c) Describe the electrochemistry of solution. **5**

Or

(a) Define activity and activity coefficient. Describe any method for the determination of activity and activity coefficient. **10**

(b) Derive Debye-Huckel limiting law. **5**

(c) Calculate ionic strength of a solution containing 0.01M K_2SO_4 and 0.1M KCl **5**

Unit IV

4. **(a))** Discuss the kinetics of chain reaction between hydrogen and bromine. Compute the activation energies for elementary processes occurring in the $H_2 + X_2 \rightarrow 2HX$ reaction. (X=Cl, Br, I). **10**

(b) Discuss all about the oscillatory reactions. **5**

(c) Is it true that the pre-exponential factor of Arrhenius equation gets physical meaning on developing collision theory? **5**

Or

(a) What is the relationship between Transition state theory and statistical mechanics? Derive Transition state theory. **10**

(b) Calculate the room temperature ratio of rate constants for two reactions that have the same A value but have E_a values that differ by 1.0 kcal/mol. (T=298K) **5**

(c) Discuss various methods of determination of rate law. **5**
