

**D.K.M. COLLEGE FOR WOMEN (AUTONOMOUS), VELLORE-1**  
**PHYSICAL CHEMISTRY-I**

**UNIT-I      Thermodynamics – I**

**Section-A (6 Marks)**

1. Derive an expression for variation on chemical potential with respect to pressure and temperature.
2. Define fugacity in term of Lewis Randell method.
3. Explain the approximation method of chemical potential.
4. Derive an expression for the Gibbs Duhem equation.
5. Derive an expression for Gibbs Duhem Mergules equation.
6. Deduce the Partial molar volume and Partial molar heat content.
7. Explain the compressibility data for fugacity.

**Section-B (15 Marks)**

8. Explain in detail about the thermodynamics of ideal and non ideal binary solutions.
9. Derive an expression for method of intercepts and graphical method of fugacity.
10. How will you determine the fugacity using Vander Waals equation of state.
11. Explain the variation of fugacity with temperature and pressure.
12. Explain the partial molar properties for free energy and enthalpy and entropy.

**UNIT –II      THERMODYNAMICS-II**

**Section-A (6 Marks)**

1. Write a short note on excess functions for non-ideal solutions.
2. Give an account for choice of standard states.
3. Explain in detail for determination of activity and activity co-efficient for electrolytes by emf and vapour measurements.

4. Explain in detail for determination of activity and activity co-efficient for electrolytes by Gibbs –Duhem equation and solubility product method  
Derive Gibbs-Margulas equation.
6. Discuss briefly on the thermodynamics of ideal binary solutions.
7. Explain the concept of activity and activity co-efficients.
8. Distinguish between ideal and non-ideal solutions.

**Section-B (15 Marks)**

9. Explain the terms activity and activity coefficient. How will you determine the activity of a non-electrolyte?
10. Apply solubility product method and emf measurements methods for determining activity and activity co-efficient of electrolytes.

**UNIT -III**

**CHEMICAL KINETICS-I**

**Section-A (6 Marks)**

1. Write a short note on effect of temperature on reaction rates.
2. Write a short note on Lewis rigid sphere theory.
3. Give an account for the estimation of free-energy and enthalpy.
4. Write a short note on entropy of activation and their significance.

**Section-B (15 Marks)**

5. Derive Eyring equation.
6. Write a short notes on reactions in solution.
7. Write a short notes on Bronsted catalysis law.
8. Explain in detail about the collision theory on reaction rate.
9. Explain in detail about the Molecular beam method in determination of rate constant.

10. Discuss briefly about the ARRT.
11. Discuss in detail about the acid-base catalysis and explain its mechanism

#### **UNIT-IV**

##### **Fast reactions and Group theory**

##### **Section-A (6 Marks)**

1. What are reducible and irreducible representations? Explain.
2. Write the direct product representations.
3. Discuss in detail about the symmetry elements and symmetry operations using suitable examples?
4. Define the term symmetry, symmetry elements and symmetry operations.
5. Explain in detail about flash photolysis and stopped flow method.
6. A group has the following irreducible representations  $A_1, A_2, B_1, B_2, E_1, E_2$ 
  - i. What is the order of the group?
  - ii. How many classes are in the group?
7.  $D_5$  has four classes and the order of the group is 10.
  - i. How many irreducible representations are possible.
  - ii. What is the dimension of each.
8. Write a short on Luminescence and energy transfer process.
9. Determine the symmetry point groups of the following molecules.
  - i.  $C_6H_6$
  - ii. Staggered ferrocene.
  - iii. Pyridine
10. Discuss the T-jump method of fast reactions
11. Discuss in detail about the symmetry elements and symmetry operations using suitable examples?
12. Write a short note on direct product representation

13. List the symmetry elements in the following molecules: Staggered ferrocene, Pyridine, trans-dichloro ethylene

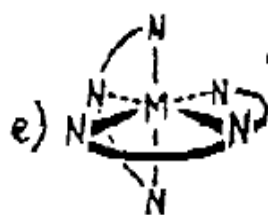
14. Identify the point groups for

(a) trans-PtCl<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> (square planar Pt; ignore the H's)

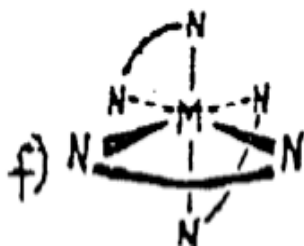
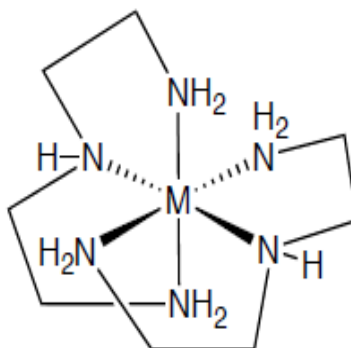
(b) cis-[CrCl<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup> (octahedral Cr; ignore the H's)

(c) XeF<sub>2</sub>

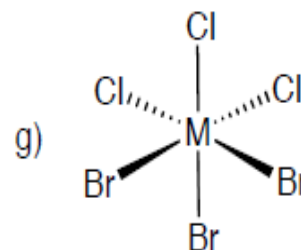
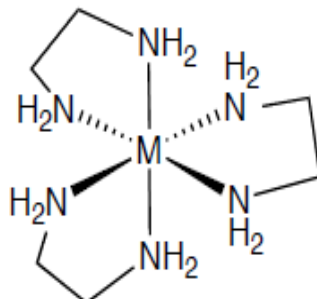
(d) XeF<sub>4</sub>



or



or



1. How will you systematically identify point group of a molecule?
2. Explain direct product and irreducible representations.

### Section-B (15 Marks)

1.a. Give an brief account on flash photolysis.

b. Predict the point group and write the symmetry operations for SF<sub>6</sub> and XeF<sub>6</sub>

c.Explain Abelian and sub group.

2. Discuss in detail about the following methods in detail

- i. Stopped flow method
- ii. Flash photolysis method
- iii. Pressure jump method

3. Predict the point group of the following compounds.

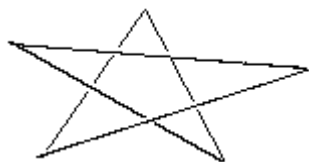
a) Eclipsed ferrocene.

b)  $\text{H}_3\text{BO}_3$

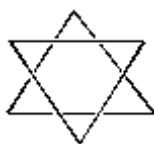
c)  $\text{PCl}_5$

d) Write a note on direct product representation.

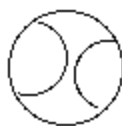
4. Identify the point group of each of the following pictures. (5)



five-pointed star



Star of David



baseball



pencil

b. Write the group multiplication table for the abelian group and explain the rules that are obeyed in abelian group. (8)

c. Define symmetry elements. (2)

5.. a. Construct the group multiplication table for  $\text{C}_{3v}$  point group. (7)

b. What is meant by similarity transformation? Explain. (5)

c. What is meant by abelian group? (3)

6. Give the point groups of these molecules, using VSEPR to find their structure if needed

i. benzene

iii. 1,2-dichlorobenzene

v. 1,3,5-trichlorobenzene

vii.  $\text{B}_2\text{Cl}_4$  (planar, with a B-B bond)

ix.  $[\text{SnCl}_3]^-$

x. cis and trans  $\text{N}_2\text{F}_2$  (planar, with N-N double bonds)

xi. NSF

ii. chlorobenzene

iv. 1,4-dichlorobenzene

vi. 1,3-dichlorobenzene

viii.  $[\text{InCl}_5]^{2-}$

xii.  $\text{I}_3^+$  and  $\text{I}_3^-$

## UNIT-V

## APPLICATIONS OF GROUP THEORY

### Section-A (6 Marks)

1. State and explain orthogonality theorem
2. Group theoretically deduce the hybridization scheme in  $\text{CH}_4$  molecule.
3. Discuss the symmetric selection rules of IR spectra
4. Construct the character table for  $\text{C}_{2v}$  point group.
5. Discuss in detail about the vibrational modes in water molecule.
6. Discuss the symmetric selection rules of IR and Raman spectra.
7. Apply group theory to find the allowed and forbidden electronic transitions in formaldehyde.
8. Systematically determine the symmetry types of normal modes in ammonia

### Section-B (15 Marks)

1. Obtain the character table for  $\text{C}_{3v}$  point group and arrive at the type of hybridization scheme in  $\text{CH}_4$  molecule.
2. Predict the electronic transition in formaldehyde and prove  $\text{vib}=2\text{A}_1+\text{B}_2$  for water molecule.
3. a. Discuss about orthogonality theorem and its consequences. (8)  
b. Determine the vibrational modes for  $\text{PCl}_5$  molecule. (7)
4. Reduce the following representations to their corresponding irreducible representations.

$\text{C}_{6v}$	E	$2\text{C}_6$	$2\text{C}_3$	$\text{C}_2$	$3\sigma_v$	$3\sigma_d$
$\Gamma$	7	1	1	1	-1	-3

$\text{D}_{2d}$	E	$2\text{S}_4$	$\text{C}_2$	$2\text{C}_2'$	$2\sigma_d$
$\Gamma$	5	1	-3	-1	-1

$\text{T}_d$	E	$8\text{C}_3$	$3\text{C}_2$	$6\text{S}_4$	$6\sigma_d$
$\Gamma$	8	-1	0	-2	2

5. State and explain the mutual exclusion principle. Construct the  $\text{C}_{2h}$  character table and show how this point group confirms the mutual exclusion principle.

6. Explain how will you deduce group theoretically the vibration modes in  $\text{CH}_4$ .
7. A. Obtain the symmetries of normal modes of vibration in tetrahedral  $\text{BH}_4^-$ . Discuss the differences in IR and Raman spectra of the vibrational modes in the ion.  
b. obtain the symmetries of the vibrational modes in water and ammonia.
8. What are the elements of symmetry present in trans-1,3-butadiene?  
Obtain the reducible representation for the four carbon pi orbitals.