Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic table/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico-Chemical Constants

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avogadro Number</td>
<td>$N = 6.022 \times 10^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Boltzmann Constant</td>
<td>$k = 1.38 \times 10^{-16}$ erg K$^{-1}$ molecule$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$= 1.38 \times 10^{-23}$ J K$^{-1}$ molecule$^{-1}$</td>
</tr>
<tr>
<td>Planck Constant</td>
<td>$h = 6.626 \times 10^{-27}$ erg s</td>
</tr>
<tr>
<td></td>
<td>$= 6.626 \times 10^{-34}$ J s</td>
</tr>
<tr>
<td>Electronic Charge</td>
<td>$e = 4.803 \times 10^{-10}$ esu</td>
</tr>
<tr>
<td></td>
<td>$= 1.602 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>1 eV</td>
<td>$= 23.06$ k cal mol$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$= 1.602 \times 10^{-12}$ erg</td>
</tr>
<tr>
<td></td>
<td>$= 1.602 \times 10^{-19}$ J</td>
</tr>
<tr>
<td></td>
<td>$= 8065.5$ cm$^{-1}$</td>
</tr>
<tr>
<td>Gas Constant</td>
<td>$R = 8.314 \times 10^{7}$ erg K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$= 8.314$ J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$= 1.987$ cal K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>Faraday Constant</td>
<td>$F = 96487$ C equiv$^{-1}$</td>
</tr>
<tr>
<td>Speed of light</td>
<td>$c = 2.997 \times 10^{10}$ cm s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$= 2.997 \times 10^{8}$ m s$^{-1}$</td>
</tr>
<tr>
<td>1 cal</td>
<td>$= 4.184 \times 10^{7}$ erg</td>
</tr>
<tr>
<td></td>
<td>$= 4.184$ J</td>
</tr>
<tr>
<td>1 amu</td>
<td>$= 1.673 \times 10^{-27}$ kg</td>
</tr>
<tr>
<td>Bohr magneton</td>
<td>$\beta_c = -9.274 \times 10^{-24}$ J T$^{-1}$</td>
</tr>
<tr>
<td>Nuclear magneton</td>
<td>$\beta_n = 5.051 \times 10^{-27}$ J T$^{-1}$</td>
</tr>
<tr>
<td>Mass of an electron</td>
<td>$m_e = 9.11 \times 10^{-31}$ kg</td>
</tr>
</tbody>
</table>

P.T.O.
SECTION - 1

Q1) Attempt the following: [10]

a) What is fugacity? Write the expression for chemical potential in terms of fugacity.

b) State the expression for Laplacian operator.

c) What is the physical significance of DG?

d) What evidence supports the idea that electromagnetic radiation is
   i) wave like
   ii) particle like?

e) Give the expression for Boltzman distribution law.

Q2) Attempt any two of the following: [10]

a) What is partial molar volume? Describe one method for the determination of partial molar volume.

b) Derive the expression for distribution of particles in an ensemble on the basis of Fermi-Dirac statistics.

c) Show that $\Delta E \to 0$ as $n \to \infty$, in spite of the relation $E_n = \frac{n^2 h^2}{8ma^2}$ for the energy levels for a particle in a box.

d) What is tunneling effect? Explain the term decay length.

Q3) Solve any one of the following: [5]

a) The moment of inertia of the oxygen molecule is $1.9373 \times 10^{-46}$ kg m². Calculate the rotational partition function for the gas at 30°C and 1 bar.

b) When lithium is irradiated with light of wavelength 300 nm electrons having kinetic energy $2.935 \times 10^{-19}$J are ejected. Calculate the threshold frequency and work function of Lithium.
SECTION - II

Q4) Attempt the following : [10]

a) For a reversible reaction, show that $t = 1/k_i$ where $k_i$ is the forward rate constant.

b) For the reaction $2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}$, the experimental rate law is

$$-\frac{d[\text{NO}_2]}{dt} = k[\text{NO}_2][\text{F}_2].$$

Propose a mechanism for the reaction.

c) Write the weaknesses of the collision theory.

d) What is ionic strength? Calculate the ionic strength of 0.1m kcl.

e) State the expression for the michaelis menten equation. Draw line weaver - Burk plot for an enzyme catalysed reaction.

Q5) Attempt any two of the following : [10]

a) What are consecutive reactions? Show that in a consecutive reaction, the rate of formation of product depends on the rate at which the intermediate is formed.

b) For the following cyclic equilibrium reaction

![Diagram]

show that $k_1 \times k_3 \times k_5 = k_2 \times k_4 \times k_6$

c) Derive Eyring’s equation using assumptions in the transition state theory.

d) Discuss the competitive inhibition in enzyme catalysed reactions.
Q6) Solve any one of the following:

a) The enzymatic conversion of a substrate at 25°C has a Michaeli’s constant 0.035 mol L⁻¹. The rate of the reaction is $1.2 \times 10^{-3}$ M.s⁻¹ when the substrate concentration is 0.106 M. What is the rate of enzymolysis if the initial concentration of the enzyme is $2.5 \times 10^{-3}$ M?

b) For a reaction $2HI \rightleftharpoons H_2(g) + I_2(g)$, the energy of activation is 44.6 kcal/mole. The collision diameter ($\sigma$) of HI is $3.58 \times 10^{-8}$ cm². Find the specific rate of the reaction at 508°C using the collision theory.
5123]-102

M.Sc. - I (Semester - I)

INORGANIC CHEMISTRY

CHI - 130 : Molecular Symmetry and Chemistry of P-block Elements

(2013 Pattern) (Old - 5 Credit System)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:

1) All questions are compulsory.
2) Answer to the two sections should be written in separate answer books.
3) Figures to the right indicate full marks.
4) Use of log tables / character tables and calculator is allowed.

SECTION - I

Q1) Answer the following : [10]

a) Define plane of symmetry and draw the planes of symmetry in BF$_3$ molecule.

b) Find improper axis of rotation in the following molecule :
   i) CCl$_4$
   ii) C$_2$H$_6$ (eclipsed)

c) List out symmetry elements of the molecule and classify into appropriate point group i) SOCl$_2$

d) Find whether the following operation is commutative or non-commutative in NH$_3$ molecule i) $C_3^2 \times \sigma_v$

e) Find the order of group and number of classes in CHCl$_3$. 

P.T.O.
Q2) Attempt any two of the following:

a) Prove that $S_n^{2n} = E$ using suitable example.

b) Derive the character table for $H_2O_2$ (trans) molecule.

c) Label the following irreducible representations with appropriate Mulliken symbols and justify.

<table>
<thead>
<tr>
<th>$D_2h$</th>
<th>E</th>
<th>$C_2(z)$</th>
<th>$C_2(y)$</th>
<th>$C_2(x)$</th>
<th>i</th>
<th>$\sigma_{(xy)}$</th>
<th>$\sigma_{(xz)}$</th>
<th>$\sigma_{(yz)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$T_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$T_3$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$T_4$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$T_5$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

d) Explain all the symmetry elements and classify it into appropriate point group: Eclipsed Ferrocene.

Q3) Attempt any one of the following:

a) Find irreducible representations of vibrational modes in $CO_3^{2-}$ ion. (Given character table)

b) Find out the normalized SALC using projection operator $B_1$ operates on $\phi_1$ orbital of $NO_2^-$ ion.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2^z$</th>
<th>$\sigma_{xz}$</th>
<th>$\sigma_{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

SECTION - II

Q4) Answer the following:

a) What are electron rich hydrides? Explain with example.

b) What are the types of crown ethers used in extraction of alkali and alkaline earth metals?
c)  Borazine is inorganic benzene, explain with structure.

d)  What are allotropes of carbon? Draw the structure of fullerene.

e)  Mention the types of oxoacids of halogens with one example each.

Q5) Attempt any two of the following: [10]

a)  Write a note on activation of nitrogen.

b)  Give an account of molecular sieves.

c)  Write a note on metal fullerenes.

d)  Write a note on - oxoacids of chlorine.

Q6) Attempt any one of the following: [5]

a)  Explain the structure and bonding in

   i)  \( \text{CH}_4 \)

   ii) \( \text{IF}_5 \)

b)  Draw the structures of following:

   i)  \( \text{B}_5\text{Hg} \)

   ii) \( \text{BrF}_5 \)

   iii) \( [\text{Cl}_2\text{PN}]_3 \)

   iv) \( \text{Al}_2(\text{ph})_2(\text{Et})_4 \)

   v)  \( \text{N}_2\text{O}_5 \)
Given:

Character table for $D_3h$ point group:

<table>
<thead>
<tr>
<th>$D_3h$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2'$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A_1''$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

$x^2 + y^2, z^2$

$R_z$

$(x, y)$

$(x^2 - y^2, xy)$

$z$

$(x, y)$

$(xz, yz)$
M.Sc. (Part - I) (Semester - I)
ORGANIC CHEMISTRY
CHO - 150 : Basic Organic Chemistry
(2013 Pattern) (5 Credits)

Time : 3 Hours
Max. Marks : 50

Instructions to the candidates:
1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Answers to the two sections should be written in separate answer books.

SECTION - I

Q1) Attempt any three of the following:

a) Justify the pKa of the following compounds.

\[
\text{pKa} \rightarrow 4.76 \quad 2.45 \quad 2.85 \quad 0.70
\]

b) Discuss structures of carbocation and carbon free radical with suitable examples.

c) Assign E/z configurational labels to the following compounds.

\[
\text{i)} \quad \text{ii)}
\]

d) Justify pKa of the following compounds.

\[
\text{pKa} \rightarrow 4.63 \quad 5.25 \quad 11.12
\]

P.T.O.
Q2) a) Write short notes on (any two):
   i) Regioselectivity.
   ii) Stability of carbocation.
   iii) Inductive effect.

b) Assign R/s configurational labels to the following:

Q3) Attempt any four of the following:

a) Assign Re/si face labels to the following:

b) Convert Fischer projection to Newman in the above.

c) Assign pro - R and pro - S labels to H_A & H_B

d) Trans - 1 - t - butyl, 4 - methyl cyclohexane predominantly exists in e,e conformation.

e) Comment on optical activity of the following compound.
SECTION - II

Q4) Attempt any three of the following:

a) Inversion of configuration is observed when Carboxyl group of acids is converted in to acid chloride using thionyl chloride & Pyridine.

b) Compare Saytzeff's and Hofman's elimination.

c) Reaction of Propyl bromide with toluene in presence of Al Br₃ gives 4-methyl cumene explain.

d) Sandmeyer reaction is a example of Ar SN', explain it with suitable example.

Q5) Suggest the mechanism (any four):

a) \[
\begin{align*}
\text{CH}_3-\text{CH}_2-\text{C}=\text{O} \quad &\xrightarrow{\text{AcOH}} \quad \text{CH}_3-\text{CH}_2-\text{COCH}_3 \\
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_2=\text{CH} \quad &\xrightarrow{\text{HCl}} \quad \text{HOCH}_2-\text{CH}_2-\text{CH}_2-\text{OH} \\
\end{align*}
\]

c) \[
\begin{align*}
\text{C}_6\text{H}_5 \quad &\xrightarrow{\text{CH}_3\text{SO}_4, \Delta} \quad \text{C}_6\text{H}_5-\text{CH}_2-\text{OH} \\
&\xrightarrow{\text{NaOH}, \Delta} \quad \text{C}_6\text{H}_5-\text{CH}_2-\text{OH} \\
&\xrightarrow{\text{H}^+} \quad \text{C}_6\text{H}_5-\text{H}^+ \\
\end{align*}
\]

d) \[
\begin{align*}
\text{Me}-\text{C}=\text{CH}_2-\text{OBS} \quad &\xrightarrow{\text{AcOH}} \quad \text{Me}-\text{C}=\text{CH}_2-\text{OAc} \\
\end{align*}
\]

e) \[
\begin{align*}
\text{C}_6\text{H}_5-\text{Cl} \quad &\xrightarrow{\text{NaNH}_2} \quad \text{C}_6\text{H}_5-\text{NH}_2 + \text{C}_6\text{H}_5-\text{NH}_2 \\
\end{align*}
\]
Q6) a) Attempt any two:

i) Effects of solvent and attacking nucleophile on $S_{N,1}$ reaction.

ii) Write a note on iPSO reaction.

iii) Cyclopropenyl anion is not aromatic but cyclopropenyl cation is.

b) Predict the products in the following:

\[ 	ext{[Image: Chemical structures and reactions]} \]
[5123]-104
M.Sc. - I (Semester - I)
ANALYTICAL CHEMISTRY
CHA - 190: Safety in Chemical Laboratory & Good Laboratory Practices
(2013 Pattern) (Credit System) (5 Credit)
Time: 3 Hours]  [Max. Marks : 50

Instructions to the candidates:
1) Answer to two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.

SECTION - I

Q1) Attempt the following: [10]
   a) What is chemical safety?
   b) Explain in short "Biological hazards."
   c) How will you prepare a safety report to avoid chemical accidents while working in Laboratory?
   d) Give any two examples for corrosive & carcinogenic chemicals.
   e) How to avoid eye injury in Laboratory?

Q2) Answer any two of the following: [10]
   a) Write a note on PPE.
   b) What is chemical waste? Give classification of chemical waste.
   c) Write a note on storage condition.
   d) Explain different types of hazards in chemical laboratory.

P.T.O.
Q3) Answer any one of the following:

   a) Give the history & importance of safety & health in laboratory.
   b) Write a note on need for Globally Harmonized system for SDS.

SECTION - II

Q4) Attempt the following:

   a) Write any two Do's & Don'ts in laboratory.
   b) What is ISO & NABL accreditation?
   c) Distinguish between dry & wet fire extinguishers.
   d) State the principle of GLP.
   e) What is OSHA Laboratory standard?

Q5) Answer any two of the following:

   a) Write a note on action to be taken in case of chemical spills on clothes in laboratory.
   b) What are the different types of fire extinguishers? State their method of use.
   c) According to SOP's what precautions should be taken in the laboratory to avoid accidents?
   d) Explain in detail hazardous & non-hazardous waste.

Q6) Answer any one of the following:

   a) Write a short note on - Disposal methods of hazardous chemicals.
   b) Define toxic, hazardous explosive flammable & harmful chemicals. Mention different symbols used on chemical containers.
[5123]-201
M.Sc. - I (Semester - II)
PHYSICAL CHEMISTRY
CHP - 210 : Fundamentals of Physical Chemistry - II
(2013 Pattern) (5 Credit)

Time : 3 Hours]

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right indicate full marks.
4) Use of logarithmic table / calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

**Physico - Chemical Constants**

1. Avogadro Number
   \[ N = 6.022 \times 10^{23} \text{ mol}^{-1} \]

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   \[ k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \]

3. Planck Constant
   \[ h = 6.626 \times 10^{-27} \text{ erg s} = 6.626 \times 10^{-34} \text{ J s} \]

4. Electronic Charge
   \[ e = 4.803 \times 10^{-10} \text{ esu} = 1.602 \times 10^{-19} \text{ C} \]

5. 1 eV
   \[ = 23.06 \text{ k cal mol}^{-1} = 1.602 \times 10^{-12} \text{ erg} = 1.602 \times 10^{-19} \text{ J} = 8065.5 \text{ cm}^{-1} \]

6. Gas Constant
   \[ R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \]

7. Faraday Constant
   \[ F = 96487 \text{ C equiv}^{-1} \]

8. Speed of light
   \[ c = 2.997 \times 10^{10} \text{ cm s}^{-1} = 2.997 \times 10^{8} \text{ m s}^{-1} \]

9. 1 cal
   \[ = 4.184 \times 10^{7} \text{ erg} = 4.184 \text{ J} \]

10. 1 amu
    \[ = 1.673 \times 10^{-27} \text{ kg} \]

11. Bohr magneton \( \beta_{c} \)
    \[ \beta_{c} = -9.274 \times 10^{-24} \text{ J T}^{-1} \]

12. Nuclear magneton \( \beta_{n} \)
    \[ \beta_{n} = 5.051 \times 10^{-27} \text{ J T}^{-1} \]

13. Mass of an electron \( m_{e} \)
    \[ m_{e} = 9.11 \times 10^{-31} \text{ kg} \]

P.T.O.
SECTION - I

Q1) Attempt the following : [10]
   a) Give the principle of ESR spectroscopy.
   b) Pure rotational Raman Spectra of linear molecule exhibit first line at 6B cm⁻¹ but remaining at 4B cm⁻¹. Explain.
   c) How electronically excited molecule loses its energy by phosphorescence.
   d) What is Fellget advantage in FTIR?
   e) Explain any two factors which affect the width of spectral lines.

Q2) Attempt any two of the following : [10]
   a) How does optics of IR spectroscopy differ from Raman spectroscopy? Discuss the merits and demerits of Raman spectroscopy.
   b) Discuss rotational fine structure of electronic - vibration transition.
   c) Explain photoelectron spectroscopy. Why is high vaccum needed for its study?
   d) Explain classical theory of Raman effect.

Q3) Solve any one of the following : [5]
   a) Find the value of rotational constant for the molecule Br²⁹F¹⁹ if the most intense spectral line at 300k is for the transition J=17→J=18.
   b) The rotational constant for the V=0 state of the molecule is 10 cm⁻¹ and V=1 state is 9.5 cm⁻¹. Estimate the rotational constant in the state V = 2.

SECTION - II

Q4) Attempt the following : [10]
   a) Write any secular determinant for ethylene molecule.
   b) Draw bonding and anti-bonding wave functions for H₂ molecule using valence bond theory.
   c) What are Weiss indices?
d) Give preparation of $^{22}$Na isotope.

e) Give the principle of isotope dilution technique.

**Q5** Attempt any two of the following: [10]

a) Explain the Huckel theory of cyclobutadiene.

b) Discuss zone diffusion technique to calculate diffusion coefficient.

c) Explain the use of radio isotopes to determine the solubility of sparingly soluble salt.

d) Derive the expression for normalization constant for H$_2$ molecule using molecular orbital theory.

**Q6** Solve any one of the following: [5]

a) Miller indices of the plane of a crystal are 436. Calculate the intercept on crystallographic axes.

b) The half-life period of a radio-element is 24.5 minutes. How much of it would be left after 30 minutes, if the initial amount of the radioelement is 1g.
[5123]-202
M.Sc. - I (Semester - II)
INORGANIC CHEMISTRY
CHI - 230: Coordination and Bioinorganic Chemistry
(2013 Pattern) (5 Credits)

Time : 3 Hours]

Instructions to the candidates:
1) All questions are compulsory.
2) Answers to the two sections should be written in separate answer book.
3) Figures to the right indicate full marks.
4) Given: Atomic number: Co = 27, Gd = 64, Cr = 24, Fe = 26, Ni = 28.

SECTION - I

Q1) Answer the following: [10]

a) How would you account the magnetic moment listed against the following complex. \([\text{Ni(NH}_3\text{)}_6]SO_4\) \(\mu_{\text{obs}} = 2.84\) B.M.

b) Arrange the following in increasing order of energy and justify your answer
\(^4\text{f}, \text{ }^3\text{p}, \text{ }^1\text{G}, \text{ }^6\text{H}, \text{ }^3\text{I}\) and \(^6\text{D}\).

c) Give the ground state term symbols for the following ions:
   i) \(\text{Co}^{2+}\)
   ii) \(\text{Gd}^{3+}\)

d) Predict the expected electronic transitions in \([\text{Fe(CN)}_6]^{3-}\).

e) Classify the following transitions as arbitrarily allowed, vibronically allowed
   and Forbidden in octahedral complex. Justify your answer.
   i) \(\text{Eg} \rightarrow \text{Eg}\)
   ii) \(\text{T}_1\text{g} \rightarrow \text{T}_2\text{g}\)

P.T.O.
Q2) Answer any two of the following: [10]

a) Assign the spin multiplicities to the states arising from \((t_{2g})^3\) configuration when infinitely strong octahedral field is relaxed to strong field using Bethe's method of desending symmetry, correlation table and direct product table.

b) Write note on Tanabe - Sugano diagram.

c) Prepare micro state table for s'd' configuration and hence derive the allowed R.S. term for the same.

d) Give the splitting of \(4F\) term in weak cubic field using character table for pure rotational point group '0'.

Q3) Answer any one of the following: [5]

a) For hexa aqua Co(II) complex ion two absorption bands are observed at 16050 cm\(^{-1}\) and 19400 cm\(^{-1}\). Determine the third absorption band, crystal field parameters and intertronic repulsion parameter. Comment on Nepheauxetic ratio.

b) For [Cr(OX)\(_3\)]\(^{3-}\) complex ion the \(\mu_{\text{eff}}\) is 3.80 B.M. The \(\gamma_1\) transition of this complex is observed at 17000 cm\(^{-1}\). Calculate the spin orbit coupling constant.

SECTION - II

Q4) Attempt the following: [10]

a) Discuss the path ways of absorption of metal ion by Cell.

b) What is the role of Zn ion in zinc - finger.

c) Explain the importance of corrin as ligand in biosystem.

d) Why transition metal ions are associated with metallo enzymes?

e) What is bioinorganic chemistry? List the bioessential elements and discuss their functions in biosystem.
Q5) Write note on any two of the following:

a) Iron - sulphur cluster.

b) The Hard - Soft Acid - Base concept.

c) Metals in medicine.

d) Voltage gated sodium channel.

Q6) Attempt any one of the following:

a) Match the following:

i) Zn \hspace{1cm} \text{Nitrogen Fixation}

ii) Mo \hspace{1cm} \text{Structure hydrolase}

iii) Cu \hspace{1cm} \text{Photo synthesis}

iv) Co \hspace{1cm} \text{Alkyl group transfer}

v) Mg \hspace{1cm} \text{dioxygen transport}

b) Draw the structures of:

i) Haemoglobin

ii) Uracil

iii) Vitamin $B_{12}$

iv) 4Fe - $\mu$ S

v) Flavin
DIRECT PRODUCTS

1. Groups of the form $G \times i$ or $G \times \sigma_h$:
   The $g, u$ or $\tau, \tau'$ additions to the IR symbols in these groups satisfy
   $g \times g = u \times u = g, g \times u = u, \tau \times \tau' = \tau', \tau' \times \tau = \tau'$.

2. Products of the form $A \times A, B \times B, A \times B$:
   For all groups:
   Letter symbols: $A \times A = A, B \times B = A, A \times B = B$.
   Subscripts: $1 \times 1 = 1, 2 \times 2 = 1, 1 \times 2 = 2$.
   except for the B representations of $D_2$ and $D_{2h}$ where
   $B \times B = B$ and $1 \times 2 = 3, 2 \times 3 = 1, 3 \times 1 = 2$.

3. Products of the form $A \times E, B \times E$:
   (a) For all groups: $A \times E_k = E_k$ irrespective of the suffix on $A$.
   (b) For all groups except $D_{6h}, D_{4d}, S_8$:
        $B \times E_1 = E_2, B \times E_2 = E_1$
        irrespective of the suffix on $B$. (If the group has only one $E$ representative
        put $E_1 = E_2 = E$.)
   (c) For $D_{4h}$:
        $u \times E_1 = E_1, B \times E_2 = E_4, B \times E_3 = E_3, B \times E_4 = E_2, B \times E_2 = E_1$
        irrespective of the suffix on $B$.
   (d) For $D_{4d}, S_8$:
        $B \times E_1 = E_1, B \times E_2 = E_2, B \times E_3 = E_1$
        irrespective of the suffix on $B$.

4. Products of the form $E \times E$:
   (For groups which have A, B or E symbols without suffixes put $A_1 = A_2 = A$ etc. in the equations below)
   (a) For $O_h, O, T_d, D_{6h}, D_6, C_{6v}, C_{6h}, C_6, S_6, D_{3h}, D_{3h}, D_3, C_{3v}, C_{3h}, C_3$:
        $E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + E_1, E_1 \times E_2 = B_1 + B_2 + E_1$.
   (b) For $D_{4h}, D_4, C_{4v}, C_{4h}, C_4, S_4, D_{2d}$:
        $E \times E = A_1 + A_2 + B_1 + B_2$.
   (c) For $D_{4d}$:
        $E_1 \times E_1 = E_2 \times E_2 = A_1 + A_2 + E_2$,
        $E_2 \times E_2 = E_4 \times E_4 = A_1 + A_2 + E_4$,
        $E_3 \times E_3 = A_1 + A_2 + B_1 + B_2$.
        $E_1 \times E_2 = E_4 \times E_3 = E_1 + E_3, E_1 \times E_3 = E_2 \times E_2 = E_3 + E_4$,
        $E_1 \times E_4 = E_2 \times E_3 = E_3 + E_3, E_2 \times E_3 = E_3 \times E_4 = E_4 + E_4$,
        $E_1 \times E_2 = B_1 + B_2 + E_4, E_2 \times E_4 = B_1 + B_2 + E_2$.
(d) \( D_{2h}, D_{1h}, D_{1h}, C_{2v}, C_{1v}, C_{3} \):
\[ E \times E = A_1 + A_1 + E_2, \quad E_2 \times E_2 = A_1 + A_1 + E_1, \]
\[ E_1 \times E_2 = E_1 + E_2. \]
(e) For \( D_{2h}, S_6 \):
\[ E \times E_1 = E_1 \times E_1 = A_1 + A_1 + E_2, \]
\[ E \times E_2 = A_1 + A_1 + B_1 + B_2, \]
\[ E_1 \times E_2 = E_1 \times E_2 = E_1 + E_1, \quad E_2 \times E_2 = B_1 + B_2 + E_2. \]

5. Products involving the \( T \) (or \( F \)) representations of \( O \) and \( T_d \):
\[ A_1 \times T_1 = T_1, \quad A_1 \times T_2 = T_2, \quad A_2 \times T_1 = T_3, \quad A_2 \times T_2 = T_4, \]
\[ E \times T_1 = E \times T_2 = T_1 + T_2, \]
\[ T_1 \times T_1 = T_1 \times T_2 = A_1 + E + T_1 + T_2, \]
\[ T_1 \times T_2 = A_2 + E + T_1 + T_2. \]

6. The complete results for \( O \) are:

<table>
<thead>
<tr>
<th>( O )</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
<th>( E )</th>
<th>( T_1 )</th>
<th>( T_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>( A_1 )</td>
<td>( A_1 )</td>
<td>( E )</td>
<td>( T_1 )</td>
<td>( T_2 )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>( A_2 )</td>
<td>( A_1 )</td>
<td>( E )</td>
<td>( T_2 )</td>
<td>( T_1 )</td>
</tr>
<tr>
<td>( E )</td>
<td>( E )</td>
<td>( E )</td>
<td>( A_1 + A_2 + E )</td>
<td>( T_1 + T_2 )</td>
<td>( T_1 + T_2 )</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>( T_1 )</td>
<td>( T_1 )</td>
<td>( T_1 + T_2 )</td>
<td>( A_1 + E + T_1 + T_2 )</td>
<td>( A_1 + E + T_1 + T_2 )</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>( T_2 )</td>
<td>( T_1 )</td>
<td>( T_1 + T_2 )</td>
<td>( A_1 + E + T_1 + T_2 )</td>
<td>( A_1 + E + T_1 + T_2 )</td>
</tr>
</tbody>
</table>

**CORRELATION TABLE FOR GROUP \( O_{h} \)**

<table>
<thead>
<tr>
<th>( O_6 )</th>
<th>( O )</th>
<th>( T_6 )</th>
<th>( D_{2h} )</th>
<th>( D_{1h} )</th>
<th>( C_{1v} )</th>
<th>( D_{1h} )</th>
<th>( D_{2h} )</th>
<th>( C_{1h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1s} )</td>
<td>( A_{1s} )</td>
<td>( A_{1s} )</td>
<td>( A_{1s} )</td>
<td>( A_{1s} )</td>
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<td>( A_{1s} )</td>
</tr>
<tr>
<td>( T_{2} )</td>
<td>( T_{2} )</td>
<td>( T_{2} )</td>
<td>( T_{2} )</td>
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<td>( T_{2} )</td>
<td>( T_{2} )</td>
<td>( T_{2} )</td>
</tr>
</tbody>
</table>

**Character Table for \( (e) \) Rotational Group**

<table>
<thead>
<tr>
<th>( O )</th>
<th>( E )</th>
<th>( 3C_{2} (= C_{2}'') )</th>
<th>( 8C_{3} )</th>
<th>( 6C_{1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_{2} )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>( T_{1} )</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( T_{2} )</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ x^2 + y^2 + z^2 \]
\[ (2x^2 - x^2 - y^2) \]
\[ x^2 - y^2 \]
\[(x,y,z,t): (x',y',z',t')\)
M.Sc. - I (Semester - II)
ORGANIC CHEMISTRY
CHO - 250 : Synthetic Organic Chemistry and Spectroscopy
(2013 Pattern) (5 Credit)

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer book.
2) All questions are compulsory.
3) Figures to the right indicate full marks.

SECTION - I

Q1) Explain any five of the following: [10]

a) Claisen rearrangement of 2-naphthyl allyl ether yields 1-allyl-2-napthol and not 3-allyl-2-napthol.

b) 4-tert-butylcyclohexanone on reaction with NaBH₄ yields equatorial alcohol as the major product whereas tri-iso-butyl-lithium borohydride yields axial alcohol as the major product.

c) Esters on reaction with Grignard reagent give tertiary alcohols and Amides gives Ketones.

d) Sulphur yields could be used for synthesis of epoxide.

e) In catalytic reduction of nitriles to primary amines some secondary amines are also isolated.

f) Wolf Rearrangement is used to prepare higher homologue of starting acid.

Q2) Write short note on any five of the following: [10]

a) Ozonolysis

b) Favorskii rearrangement

P.T.O.
c) Use of organozinc compounds in organic synthesis.

d) Moffatt oxidation.

e) Horner - Wadsworth - Emmons modification of Wittig reaction.

f) Wolf - Kishner Reduction.

Q3) Predict the products and suggest the mechanism. (any two)  [5]

SECTION - II

Q4) Attempt any five of the following: [10]

a) Calculate the $\lambda_{\text{max}}$ for the following compounds.

b) How will you monitor the following conversion by IR?

c) How will you distinguish following compound by PMR?

[5123]-203  2
d) Explain the Bathochromic shift with suitable example.

e) Assign the IR absorption values 1720, 1769 and 1928 cm\(^{-1}\) to the following compounds with proper justification.

f) How will you differentiate the following compounds by MS?

Q5) Deduce the structure of any five of the following compounds using spectral data and justify your answer

a) M.F. : \( \text{C}_4\text{H}_4\text{O}_4\text{NCl} \)
IR : 3300, 2700, 1720, 1540, 920 cm\(^{-1}\)
PMR : 5.85 (bs, 7mm)
7.9 (d, 7mm, 7.5 Hz)
8.4 (dd, 7mm, 7.5 & 2.5 Hz)
8.65 (d, 7mm, 2.5 Hz)

b) M.F. : \( \text{C}_{10}\text{H}_{12}\text{O} \)
U.V. : 250, 262 nm.
IR : 1745 cm\(^{-1}\)
PMR : 2.10 \( \delta \) (s, 3H)
2.75 (t, 2H)
2.85 (t, 2H)
7.20 (m, 5H)

c) M.F. : \( \text{C}_9\text{H}_{12}\text{O} \)
IR : No bands above 3100 and in 2000 - 1650 cm\(^{-1}\) region.
PMR : \( \delta = 1.15 \) (3H, t, J = 7.5 Hz)
3.5 (2H, q, J = 7.5 Hz)
4.4 (2H, 5)
7.2 (5H, 5)
d)  M.F. : \( \text{C}_8\text{H}_{12}\text{O} \)
CMR : 23.5 (t), 25.6 (t), 40.1 (t), 68.7 (s), 72.8 (d), 88.4 (s)
Mass : 124 (M⁺), 123, 109, 95, 81, 68, 53, 39.
e) Using the mass peaks given below, assign correct structure from those shown below.
M/2 15(50), 41(50), 59(8), 69(100), 85(22), 100(18).

f)  M.F. : \( \text{C}_7\text{H}_{12}\text{O} \)
IR : 1742cm⁻¹
PMR : \( \delta \) : 2.6 (s, 2H)
    1.3 (t, J = 6.5 Hz, 6H)
    4.16 (q, J = 6.5 Hz, 4H)

**Q6)** Attempt any two of the following : [5]

a) Give the genesis of important ions of the following

\[ \begin{align*}
\text{[Image]} & \rightarrow 39(35), 68(100), 95(10), 121(15), 136(20) \\
\text{[Image]} & \rightarrow 79(25), 80(10), 108(100)
\end{align*} \]

b) Assign the signals to the various carbons for following compound and justify your answer

\[ \begin{align*}
\text{[Image]} & \quad 17(q), 19(q), 25(q), 26(t), 30(q), 37(t), \\
& \quad 40(t), 61(t), 125(d), 133(s).
\end{align*} \]

c) Explain with suitable example factors affecting chemical shift in PMR.

[5123]-203 4
Modern Separation Methods and Hyphenated Techniques

Time: 3 Hours

Instructions to the candidates:

1) All questions of respective section / part are compulsory.
2) Figures to right hand side indicate full marks.
3) Neat labelled diagrams must be drawn wherever necessary.
4) Use of log table / non programmable calculator is allowed.
5) Students should attempt any two parts from Part A, B, C, D, E, F and G or full paper of biochemistry (Part - B).
6) Write the answers of two parts on separate answer books.

Q1) Answer the following [10]

a) State and explain principle of gas chromatography.

b) What is gradient elution? Explain with example.

c) How is the resolving power of HPLC column increased.

 d) What is metastable ion in Mass Spectrometry?

e) What are the characteristics of an ideal detector in HPLC?

P.T.O.
**Q2)** Attempt *any two* of the following:  

a) Explain the process of photoionization and thermal ionization in MS.

b) With a suitable schematic diagram explain the function of the components of a gas chromatography setup.

c) Distinguish between Normal phase HPLC and reverse phase HPLC.

d) What is chromatography? Classify the different chromatographic techniques and give suitable explanation.

---

**Q3)** Attempt *any one* of the following:  

a) What is meant by hyphenated technique? Explain the technique of GC-MS giving suitable examples.

b) A mixture of substances A, B, C and D were analysed using T.C.D. Determine the weight percentage of each component if areas were 5.2cm², 9.1cm², 4.6cm² and 6.9cm².

Given:  

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.56</td>
</tr>
<tr>
<td>B</td>
<td>0.73</td>
</tr>
<tr>
<td>C</td>
<td>0.81</td>
</tr>
<tr>
<td>D</td>
<td>0.85</td>
</tr>
</tbody>
</table>
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[5123]-204
M.Sc. - I (Semester - II)
ANALYTICAL CHEMISTRY
Basic Biochemistry
(2013 Pattern) (5 Credits)

Time: 3 Hours] [Max. Marks: 50

SECTION - I

Q1) Answer any three of the following:

a) How is the end group of a protein determined?
b) Give the structure of Glycogen and starch.
c) Classify proteins with suitable examples.
d) Differentiate between active and passive transport of ions.

Q2) Attempt any two of the following:

a) Describe the structure and function of mitochondria and endoplasmic reticulum.
b) What are the components of cell membrane? Give the function of each.
c) Short note on Eucaryotic cell metabolism.

Q3) Attempt any two of the following:

a) Classify types of fatty acids.
b) Comment on:
   i) Lysosomes
   ii) Sickle cell anaemia.
c) Discuss the reactions of TCA cycle. Give it’s energetics.
SECTIONS - II

Q4) Answer any three of the following: [9]
   a) Classify enzymes with suitable examples.
   b) What are double reciprocal plots? Give their importance.
   c) Discuss different types of inhibition.
   d) Give a brief account of post translational modification of protein.

Q5) Attempt any two of the following: [8]
   a) What are coenzymes? Name the coenzyme derived from B complex vitamins. Discuss their biochemical role.
   b) Discuss the major structural differences between A, B and Z forms of DNA.
   c) Discuss characteristics of genetic code and give a note on wobble hypothesis.

Q6) Attempt any two of the following: [8]
   a) Comment on:
      i) Nutritional disorders (any 2)
      ii) Night blindness
   b) Give experimental proofs to support DNA replication and whether it is semiconservative.
   c) Give therapeutic uses of enzymes.
P1381

[5123]-204
M.Sc. - I (Semester - II)
ANALYTICAL CHEMISTRY
Concept of Analytical Chemistry
(2013 Pattern) (5 Credits)

Time : 3 Hours] [Max. Marks : 25

Q1) Answer the following :

a) What is determinate error? Give an example.

b) Differentiate between batch extraction and continuous extraction.

c) Explain the test of significance.

d) Calculate the proper number of significant figures in each of the following:

i) 0.00256

ii) 22.0092

e) Give any two properties of nano materials.

Q2) Attempt any two of the following :

a) Draw a neat labelled diagram of fractionating column and explain it’s principle and working.

b) Write a note on rejection of result : The Q test.

c) Explain the factors affecting solvent extraction.

d) Describe the steps involved in the sampling process.

Q3) Attempt any one of the following :

a) Write a note on salt induced precipitation of proteins.

b) The following results were obtained in the replicate determination of lead content of a blood sample : 0.613, 0.615, 0.614, 0.615 and 0.617 ppm. Calculate the mean and standard deviation of this set of data.
P1381

[5123]-204
M.Sc. - I (Semester - II)
ANALYTICAL CHEMISTRY
Industrial Methods of Analysis
(2013 Pattern) (5 Credits)

Time : 3 Hours] 

[Max. Marks : 25

Q1) Answer of the following : [10]
   a) Enlist different types of process analysers.
   b) Explain the concept of stepwise formation constants.
   c) Give two types of quality standards for laboratory.
   d) Define : Chromatography.
   e) 0.02 g NaOH is dissolved in 100 ml water. What is the concentration of solution in ppm.

Q2) Attempt any two of the following : [10]
   a) Write a note on automatic elemental analyzer.
   b) Describe stability and instability constants giving suitable examples.
   c) What is an acidic buffer? Explain it’s action giving suitable example.
   d) Give a brief account of cost and benefits of a quality system.

Q3) Answer any one of the following : [5]
   a) Define :
      i) Quality audits.
      ii) Limiting reactants.
      iii) Gram mole.
   b) Write a note on Industrial process analyser.
Q1) Answer the following : [10]

a) Determine the valence electron counts for the transition metals in the following complexes

i)  \([\text{Fe}(\text{CO}_4)]^{2-}\)

ii)  \(\text{CO}_2\) (CO)$_8$

b) Define and explain :

i) Oxidative addition.

ii) Reductive elimination.

c) What do you understand by inert and labile complexes?

d) Which of the following obey the 18e\(^-\) rule

i)  \([\text{Ni}(\text{CN}_4)]^{2-}\)

ii)  \(\text{Fe}\) (CO)$_5$

e) Predict the type of reaction.
Q2) Attempt any two of the following: [10]

a) Differentiate between associative and dissociative mechanisms in substitution reactions.

b) Write a note on hydroformylation reaction.

c) Explain the methods of synthesis of metal carbonyls.

d) Explain in detail the electron transfer reactions.

Q3) Attempt any one of the following: [5]

a) $^{13}$C NMR is a powerful technique to characterize carbonyl compounds. Explain with suitable examples.

b) Write a note on Trans effect.
P1381

[5123]-204
M.Sc. - I (Semester - II)
ANALYTICAL CHEMISTRY
Mathematics For Chemists
(2013 Pattern) (5 Credits)

Time : 3 Hours]
[Max. Marks : 25

Q1) Answer the following : [10]
   a) Give the transpose of the following matrices.
      i) \[
         \begin{bmatrix}
            6 & 3 & 8 \\
            2 & 9 & 4
         \end{bmatrix}
      \]
      ii) \[
         \begin{bmatrix}
            7 & 2 & 4 \\
            8 & 7 & 2 \\
            7 & 3 & 6
         \end{bmatrix}
      \]
   b) Give the quotient rule for differentiation.
   c) State whether the following differential equations are exact or inexact.
      i) \((x^2y+x) \, dy + (xy^2 - y) \, dx = 0\)
      ii) \(x^2dy - y^2 \, dx - xy \, dx = 0\)
   d) Define unit and diagonal matrices. Give examples.
   e) Differentiate the equation w.r.t.x. \(y = \frac{2 + x}{2 - x}\)

Q2) Attempt any two of the following : [10]
   a) Using Falk’s scheme evaluate
      i) \[
         A = \begin{bmatrix}
            2 & 4 & 6 \\
            1 & 2 & 3
         \end{bmatrix}
      \]
      \[
         x = \begin{bmatrix}
            1 \\
            4 \\
            8
         \end{bmatrix}
      \]
      \(Ax = ?\)
ii) \[ B = \begin{bmatrix} 7 & 1 & 5 \\ 2 & 4 & 6 \end{bmatrix} \]

\[ y = \begin{bmatrix} 1 \\ 5 \\ 9 \end{bmatrix} \]

b) Enlist rules of partial differentiation and give suitable examples.

c) One card is drawn from a well shuffled deck of 52 cards. Calculate the probability that the card will be:

i) a black card

ii) not a diamond

iii) a diamond

iv) not a black card

d) i) Find the determinant of:
\[
\begin{bmatrix} 4 & 8 & 2 \\ 9 & 2 & 2 \\ 6 & 3 & 4 \end{bmatrix}
\]

ii) Find the cofactor of:
\[
\begin{bmatrix} 7 & 6 & 3 \\ 5 & 1 & 2 \\ 6 & 5 & 6 \end{bmatrix}
\]

**Q3** Answer any one of the following: [5]

a) Solve the following:

i) Integrate \( \int_0^2 (x+1)(x^3 - 3) \, dx \)

ii) Find the derivative of \( x^2 - y^2 + 5x = 9y \)

b) Write a short note on Taylor and Mclaurin theorem.
P1381

[5123]-204

M.Sc. - I (Semester - II)

GENERAL CHEMISTRY

Pericyclic, Photochemistry and Free Radical Reactions

(2013 Pattern) (5 Credits)

Time : 3 Hours]  [Max. Marks : 25

Q1) Answer the following : [10]

a) What do you mean by quantum yield, explain it’s significance in photochemical reactions.

b) Irradiation of o-xylene yields a mixture of m-and p-xylenes.

c) Discuss step-wise mechanism of Antimarkownikoff’s addition with suitable example.

d) In allylic bromination NBS is used as a brominating reagent instead of Bromine.

e) Write the mechanism of claisen rearrangement with suitable examples.

Q2) Predict the product indicating mechanism in any two of the following : [10]

a) $CCl_4 + CH_2N_2 (excess)$ $\xrightarrow{hv}$ ?

b) 

\[ \text{} \xrightarrow{hv} \text{A} + \text{B} \]

c) 

\[ \text{} + \text{H} \xrightarrow{\Delta} \]

d) 

\[ \text{} \xrightarrow{\text{KOH-THF} 20^\circ C} \]
Q3) Attempt any two of the following:

a) Explain free radical axylation of aromatic rings.

b) Write a short note on Di - IT metane rearrangement.

c) Give a brief account of Norvish Type - I process.
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M.Sc. (Semester - III)
PHYSICAL CHEMISTRY
CHP - 310 : Quantum Chemistry and Solid State Chemistry
(2013 Pattern)

Time : 3 Hours

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic table, calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1. Avogadro Number \( N = 6.022 \times 10^{23} \text{ mol}^{-1} \)
2. Boltzmann Constant \( k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} \)
   \( = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \)
3. Planck Constant \( h = 6.626 \times 10^{-27} \text{ erg s} \)
   \( = 6.626 \times 10^{-34} \text{ J s} \)
4. Electronic Charge \( e = 4.803 \times 10^{-10} \text{ esu} \)
   \( = 1.602 \times 10^{-19} \text{ C} \)
5. 1 eV \( = 23.06 \text{ k cal mol}^{-1} \)
   \( = 1.602 \times 10^{-12} \text{ erg} \)
   \( = 1.602 \times 10^{-19} \text{ J} \)
   \( = 8065.5 \text{ cm}^{-1} \)
6. Gas Constant \( R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} \)
   \( = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
   \( = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \)
7. Faraday Constant \( F = 96487 \text{ C equiv}^{-1} \)
8. Speed of light \( c = 2.997 \times 10^{10} \text{ cm s}^{-1} \)
   \( = 2.997 \times 10^{8} \text{ m s}^{-1} \)
9. 1 cal \( = 4.184 \times 10^{7} \text{ erg} \)
   \( = 4.184 \text{ J} \)
10. 1 amu \( = 1.673 \times 10^{-27} \text{ kg} \)
11. Bohr magneton \( \beta_e = -9.274 \times 10^{-24} \text{ J T}^{-1} \)
12. Nuclear magneton \( \beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1} \)
13. Mass of an electron \( m_e = 9.11 \times 10^{-31} \text{ kg} \)

P.T.O.
SECTION - I

Q1) Attempt precisely the following:  

a) Explain the properties of quantum mechanical operators.  

b) Verify the commutator identity $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$.  

c) Find the term symbols for the following configuration  

i) $2p^13d^1$ and  

ii) $1S^12S^1$  

d) What is the eigen value for the function $(\sin K_1x)(\sin K_2y)(\sin K_3z)$ of operator.  

$$\nabla^2 = \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$  

e) State the variation theorem.

Q2) Attempt any two of the following:  

a) Deduce the Hückel energies for cyclobutadiene, why is the molecule not stable?  

b) Comment, giving examples on the positive or negative nature of REPE value for molecule.  

c) Explain why cyclo octatetraene is unstable but its dianion is stable and planar.  

d) What is the need of approximate methods in quantum chemistry? Compare perturbation method with variation method.

Q3) Attempt any one of the following:  

a) Formulate the total energy operators for  

i) $\text{H}_2^-$ ion and  

ii) H atom  

State the terms involved in each of these.  

b) Derive $[\hat{M}^2, \hat{M}^\pm] = 0$, for the operators $\hat{M}^\pm$.  

[5123] -301  

2
SECTION - II

Q4) Answer precisely the following :  [10]

a) What is p–n junction? How is it created?

b) Define elastic and plastic deformation.

c) What is van Arkel process?

d) Distinguish between metal, semiconductor and insulator.

e) Define

i) Nucleation and

ii) Induction period.

Q5) Answer any two of the following :  [10]

a) Sketch and explain the hysteresis loop observed for magnetization of an insulator crystal.

b) Discuss the mechanism of diffusion in solids.

c) Discuss the growth of crystal from vapour phase.

d) Write a note on photographic process.

Q6) Solve any one of the following :  [5]

a) The diffusion coefficient of Li in Ge at 500°C is \(10^{-6}\) cm\(^2\)/s. What is the distance penetrated in one and half hour?

b) A certain alkali halide (\(A^+ X^-\)) with molecular weight 74.6 has the NaCl structure. If the interionic distance \(A^+ – X^-\) is 0.32nm, calculate the density of the salt for the 0.1% Frenkel defects.

[5123] -301
[5123]-302
M.Sc. (Semester - III)
PHYSICAL CHEMISTRY
CHP-311: Nuclear, Radiation and Photo-Chemistry
(2013 Pattern) (New)

Time: 3 Hours] [Max. Marks: 50

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic tables and calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1. Avogadro Number \(N = 6.022 \times 10^{23} \text{ mol}^{-1}\)
2. Boltzmann Constant \(k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{molecule}^{-1}\)
   \(= 1.38 \times 10^{-23} \text{ J K}^{-1} \text{molecule}^{-1}\)
3. Planck Constant \(h = 6.626 \times 10^{-27} \text{ erg s}\)
   \(= 6.626 \times 10^{-34} \text{ J s}\)
4. Electronic Charge \(e = 4.803 \times 10^{-10} \text{ esu}\)
   \(= 1.602 \times 10^{-19} \text{ C}\)
5. 1 eV
   \(= 23.06 \text{ k cal mol}^{-1}\)
   \(= 1.602 \times 10^{-12} \text{ erg}\)
   \(= 1.602 \times 10^{-19} \text{ J}\)
   \(= 8065.5 \text{ cm}^{-1}\)
6. Gas Constant \(R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{mol}^{-1}\)
   \(= 8.314 \text{ J K}^{-1} \text{mol}^{-1}\)
   \(= 1.987 \text{ cal K}^{-1} \text{mol}^{-1}\)
7. Faraday Constant \(F = 96487 \text{ C equiv}^{-1}\)
8. Speed of light \(c = 2.997 \times 10^{10} \text{ cm s}^{-1}\)
   \(= 2.997 \times 10^{8} \text{ m s}^{-1}\)
9. 1 cal
   \(= 4.184 \times 10^{7} \text{ erg}\)
   \(= 4.184 \text{ J}\)
10. 1 amu
    \(= 1.673 \times 10^{-27} \text{ kg}\)
11. Bohr magneton \(\beta_c = -9.274 \times 10^{-24} \text{ J T}^{-1}\)
12. Nuclear magneton \(\beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1}\)
13. Mass of an electron \(m_e = 9.11 \times 10^{-31} \text{ kg}\)

P.T.O.
SECTION - I

Q1) Attempt the following:

a) Define the term photofission.

b) What is channeling effect?

c) Discuss the principle of PIXE technique.

d) Explain the role of moderator & coolant in reactor.

e) What are the properties of scintillator?

Q2) Attempt any two of the following:

a) Discuss the characteristics of thermal, fast & intermediate reactors.

b) Write the sequence of filling of nuclear orbitals. What is necessity of proposing spin - orbit coupling?

c) Explain ionization & X ray emission in PIXE technique.

d) Discuss the working of Li-drifted detector with schematic diagram.

Q3) Solve any one of the following:

a) Find the thickness of Cu required to reduced on activity of $\gamma$- source from 4000 cpm to 2000 cpm

Given $\mu_{\gamma} = 0.211 \text{ b/e}^0$, $\delta_{\text{Cu}} = 8.96 \text{ g/cm}^3$.

b) Calculate the energies of the two peaks in the RBS spectrum correspons to $^{28}\text{Si}$ & $^{65}\text{Cu}$, assuming an incident $^4\text{He}^+$ ions of 2 MeV energy & a scattering angle of 170°.

SECTION - II

Q4) Attempt the following:

a) State the Law of photochemical Equivalence.

b) Define the terms dark reaction and photochemical reaction. Give an example.
c) Define quantum efficiency.

d) Write the principle of chemical actinometer.

e) Define the terms Luminescence and Incandescence.

**Q5** Attempt any two of the following: [10]

a) Explain the mechanism of delayed fluorescence.

b) What are the types of electronic transitions in organic molecules? Explain the Kasha’s test for the identification of such transitions.

c) Describe the working of Ruby and Nd/YAG Laser.

d) What is meant by quenching and state its importance?

**Q6** Attempt any one of the following: [5]

a) For the photochemical reaction

$$A \rightarrow B$$

1×10⁻³ moles of B were formed on absorption of 6.62×10⁷ erg at 3600Å. Calculate the quantum efficiency.

b) Explain Jablonski diagram depicting various photophysical processes.
Physico-Chemical Methods of analysis
(2013 Pattern) (New)

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory
3) Figures to the right side indicate full marks.
4) Use of logarithmic table calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

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2) Boltzmann constant K = 1.38 × 10^{-16} \text{erg K}^{-1}\text{molecule}^{-1}
   = 1.38 × 10^{-23} \text{JK}^{-1}\text{molecule}^{-1}

3) Planck constant h = 6.626 × 10^{-27} \text{erg s}
   = 6.626 × 10^{-34} \text{J s}

4) Electronic charge e = 4.803 × 10^{-10} \text{esu}
   = 1.602 × 10^{-19} \text{C}

5) 1 eV = 23.06 k \text{cal mol}^{-1}
   = 1.602 × 10^{-12} \text{erg}
   = 1.602 × 10^{-19} \text{J}
   = 8065.5 \text{cm}^{-1}

6) Gas constant R = 8.314 × 10^{7} \text{ergK}^{-1}\text{mol}^{-1}
   = 8.314 \text{JK}^{-1}\text{mol}^{-1}
   = 1.987 \text{cal K}^{-1}\text{mol}^{-1}

7) Faraday constant F = 96487 \text{C equiv}^{-1}

8) Speed of light c = 2.997 × 10^{10} \text{cm s}^{-1}
   = 2.997 × 10^{8} \text{m s}^{-1}

9) 1 cal = 4.184 × 10^{7}\text{erg}
   = 4.184 \text{J}

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11) Bohr magneton \(\beta_e = -9.274 × 10^{-24} \text{ J T}^{-1}\)

12) Nuclear magneton \(\beta_n = 5.051 × 10^{-27} \text{ J T}^{-1}\)

13) Mass of an electron \(M_e = 9.11 × 10^{-31} \text{ kg}\)

P.T.O
SECTIONS - I

Q1) Answer precisely the following. [10]

a) Explain the ways by which an excited ion relax in ESCA technique.

b) Draw a neat labelled diagram of an ESCA spectrometer.

c) What is meant by EXAFS? Give two applications of x-ray absorption.

d) Calculate the short - wavelength cut off the lamp when an accelerating potential in an x-ray tube is 15.5 kv.

e) Explain the term thermal analysis. enlist the various methods of thermal analysis.

Q2) Answer any two of the following. [10]

a) What is x-ray fluorescence? Draw a neat labelled diagram of wavelength-dispersive and energy -dispersive instrument used for fluorescence.

b) Explain spectral splitting and chemical shift observed in ESCA technique.

c) Discuss the applications of DSC technique.

d) Describe the cylindrical mirror analyzer used in ESCA spectrometer.

Q3) Solve any one of the following. [5]

a) Gypsum showed mass loss of about 15 % of original sample mass due to complete dehydration at 170°C. Determine the number of water molecules present in gypsum.

(Given : Atomic weight of Ca = 40, s = 32, o = 16, H = 1)

b) Calculate the wavelength of x-ray photon in nanometer that was used to create inner - shell vacancy in fluorine.

(Given : $\phi$ of the spectrometer = 4.71 eV, k.E. of electron = 799v and B.E. for f = 696 eV.)
SECTION - II

**Q4)** Attempt precisely the following

1. Define singlet state, doublet state and triplet state.
2. State the characteristics of plasma.
3. State the principle of voltammetry.
4. Write the equation for limiting current an hydrodynamic voltammetry. Explain the terms in it.
5. What are the fundamental requirement to perform coulometric titrations?

**Q5)** Answer any two of the following

1. Explain liquid - phase chemiluminescence titration with a typical example.
2. Draw a neat labelled diagram of a typical plasma and show different temperature zone in it.
3. Describe controlled - potential coulometry.
4. What is polarizable electrode? Describe different electrodes used in voltammetry.

**Q6)** Solve any one of the following

1. An electro active species yielded wave with a limiting current 25.5 μA at the rotating disc electrode which was rotated at 20.0 r/s. What limiting current would be expected at 50 r/s?

2. Constant current coulometry was used to assay a solution containing Fe^{2+}. To ensure 100% current efficiency, the assay was performed in 0.1m Ce^{3+} acidic solution at the end point of titration 30ml sample, a controlled current of 6.45 mA had flowed for 185 second. Calculate the concentration of Fe^{2+} in the sample.
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M.Sc.

PHYSICAL CHEMISTRY

CHP - 313 : Polymer Chemistry

(2013 Pattern)

Time : 3 Hours

Max. Marks : 50

Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory
3) Figures to the right side indicate full marks.
4) Use of logarithmic table calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1) Avogadro Number \( N = 6.022 \times 10^{23} \text{mol}^{-1} \)
2) Boltzmann constant \( K = 1.38 \times 10^{-16} \text{erg K}^{-1} \text{molecule}^{-1} = 1.38 \times 10^{-23} \text{JK}^{-1} \text{molecule}^{-1} \)
3) Planck constant \( h = 6.626 \times 10^{-27} \text{erg s} = 6.626 \times 10^{-34} \text{J s} \)
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5) 1 e V
   \( = 23.06 \text{ k cal mol}^{-1} = 1.602 \times 10^{-12} \text{erg} = 1.602 \times 10^{-19} \text{J} = 8065.5 \text{ cm}^{-1} \)
6) Gas constant \( R = 8.314 \times 10^{7} \text{ergk}^{-1} \text{mol}^{-1} = 8.314 \text{Jk}^{-1} \text{mol}^{-1} = 1.987 \text{cal K}^{-1} \text{mol}^{-1} \)
7) Faraday constant \( F = 96487 \text{ C equiv}^{-1} \)
8) Speed of light \( c = 2.997 \times 10^{10} \text{cm S}^{-1} = 2.997 \times 10^{8} \text{ m s}^{-1} \)
9) 1 cal
   \( = 4.184 \times 10^{7} \text{erg} = 4.184 \text{J} \)
10) I amu
    \( = 1.673 \times 10^{-27} \text{kg} \)
11) Bohr magneton \( \beta_{e} = -9.274 \times 10^{-24} \text{ J T}^{-1} \)
12) Nuclear magneton \( \beta_{n} = 5.051 \times 10^{-27} \text{ J T}^{-1} \)
13) Mass of an electorn \( M_{e} = 9.11 \times 10^{-31} \text{ kg} \)
SECTION - I

Q1) Attempt the following. [10]
   a) What is (i) Thermoplastic polymer and (ii) Thermosetting polymer?
   b) Define (i) Isotactic (ii) Syndiotactic (iii) atactic configuration of polymers.
   c) What are the properties of typical elastomers?
   d) Define azeotropic copolymerization.
   e) Define the terms (i) shear thining (ii) Shear thickening.

Q2) Attempt any two of the following. [10]
   a) Describe flory - krigbaum theory of dilute polymer solution.
   b) Derive the copolymer equation starting with assumptions used.
   c) Derive the stress - strain equation for the simple stretching of an elastomer.
   d) Discuss the secondary bond force in polymers.

Q3) Attempt any one of the following: [5]
   a) Discuss flory - Huggins theory for $\Delta S$, $\Delta H$, and $\Delta G$ of polymer solutions.
   b) Write a note on vulcanisation.

SECTION - II

Q4) Attempt the following [10]
   a) Define (i) homopolymer (ii) copolymer.
   b) What are polarons and bipolarons?
   c) Define (i) fiber (ii) Staple (iii) denier (iv) tenacity
   d) What is (i) Glass transition temperature (ii) Crystalline melting point?
   e) Define molding and enlist name of different types of molding processes.
Q5) Attempt any two of the following. [10]

a) Distinguish between chain polymerisation and step polymerisation.
b) Describe the experimental method by viscosity measurements to determine the molecular weight of the polymer.
c) Discuss the properties involving large deformations in polymer solution.
d) Explain the sedimentation velocity method for molecular weight determination of a polymer solution.

Q6) Attempt any one of the following. [5]

a) A polymer with \( m = 100,000 \) obeys Mark-Houwink equation with \( K = 1 \times 10^{-4} \) and \( \alpha = 0.80 \). Huggins constant is 0.33 calculate the relative viscosity at \( c = 0.30 \) gdl

b) Calculate \( \overline{X}_n \), \( \overline{X}_w \) and the weight fraction of \( \overline{X}_n \)-mers when a step polymerisation is 95% complete.

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M.Sc. (Semester III)

PHYSICAL CHEMISTRY

CHP - 314 : Modern Trends in Physical Chemistry
(New) (2013 Pattern) (Optional)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory
3) Figures to the right side indicate full marks.
4) Use of logarithmic tables and calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

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5) 1 eV\( = 23.06 \text{k cal mol}^{-1} = 1.602 \times 10^{12} \text{erg} = 1.602 \times 10^{19} \text{J} = 8065.5 \text{cm}^{-1} \)
6) Gas constant \( R = 8.314 \times 10^{7} \text{ergK}^{-1} \text{mol}^{-1} = 8.314 \text{Jk}^{-1} \text{mol}^{-1} = 1.987 \text{cal K}^{-1} \text{mol}^{-1} \)
7) Faraday constant \( F = 96487 \text{C equiv}^{-1} \)
8) Speed of light \( c = 2.997 \times 10^{10} \text{cm S}^{-1} = 2.997 \times 10^{8} \text{m s}^{-1} \)
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12) Nuclear magneton \( \beta_n = 5.051 \times 10^{-27} \text{J T}^{-1} \)
13) Mass of an electorn \( M_e = 9.11 \times 10^{-31} \text{kg} \)

P.T.O
Section - I

Q1) Answer precisely the following.

a) Explain the term component with an example
b) Define the term phase. Give examples of single phase and two phases.
c) Write the mass balance on sodium and sulphide ions in 0.1 m NaHs.
d) Write the charge balance for a solution of NaCl.
e) What is proton condition for Na₂ CO₃.

Q2) Answer any two of the following.

a) Discuss a high boiling azeotrope with a neat labelled diagram.
b) Define 'upper consolute temperature'. Discuss the phase diagrams for palladium and palladium hydride.
c) Explain zone refining technique to get ultrapure material.
d) Calculate pH and concentration of all species in 0.1 m H₂ CO₃ [Given : ka₁ = 4.47 × 10⁻⁷, ka₂ = 5.62 × 10⁻¹¹].

Q3) Solve any one of the following.

a) Draw a logarithmic concentration diagram for 0.1 N H₃ PO₄ [Given : ka₁ = 5.89 × 10⁻³, ka₂ = 6.10 × 10⁻⁸ and ka₃ = 4.78 × 10⁻¹³]
b) The pH of 0.1 m oxalic acid solution is 7.00. Find the concentrations of H₂C₂ O₄, HC₂ O₄⁻ and C₂ O₄²⁻
   [Given : ka₁ = 5.30 × 10⁻² and ka₂ = 5.37 × 10⁻⁵]

Section - II

Q4) Answer the following.

a) Calculate the wavelength of an electron emitted in cathode ray tube operating at 10, 000V.
b) How are the secondary electrons generated in SEM?
c) How is the exciton formed in Semiconductor nanoparticles?
d) What is piezoelectric ceramics?

e) Give the principle of electron beam lithography.

Q5) Answer any two of the following [10]

a) Discuss the properties of nanomaterials.

b) Write a note on ceramics.

c) Discuss the applications of SEM.

d) Calculate the limiting resolution that can be achieved by a microscope using a wavelength 400 nm, refractive index of the medium 0.51 & the glancing angle 45°.

Q6) Answer any one of the following [5]

a) Write the applications of nanoparticles in the field of defence & space

b) What is active smart materials? Explain with two examples.
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M.Sc. - II (Semester - III)
INORGANIC CHEMISTRY
CHI - 326 : Organometallic Chemistry and Homogeneous Catalysis
(2013 Pattern)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) All questions are compulsory.
2) Neat diagram must be drawn wherever necessary.

Q1) Answer the following : [20]

a) Draw the principal coordination modes of CO ligand.

b) Write a balanced chemical equation for the synthesis of nickel carbonyls from an appropriate cyanide.

c) What is metathesis reaction? Mention different types of metathesis reaction.

d) What is the role of CO-catalyst in wacker process?

e) Discuss chemoselectivity with suitable example.

f) Why the complexes of late transition elements are used as homogeneous catalyst?

g) What do you mean by biphasic catalysis? List out various biphasic system?

h) Give properties of cyclopentadienyls compounds.

i) What are the difference and similarities between Suzuki and Heck coupling reaction?

j) Give the formal oxidation state of the metal, d-electron count, total valence electron (TVE) and the number of M-M bonds if any, for the following molecules.

i) \( \mu\text{CO-}[\text{C}n^4\text{C}_4\text{H}_4] \text{Fe (CO)}_2 \)

ii) \( \text{Ru (PPh}_3)_2\text{Cl (NO)} \).
**Q2** Answer the following (any two) [10]

a) Explain the interdependence of inorganic and organo - metallic materials in the environment.

b) Give the methods for the preparation of metal cycloheptatrienyls compounds.

c) Discuss NMR of the following fluxional molecules.
   i) $\text{Fe}_2\,(\text{CO})_4(\eta^5 - \text{C}_5\text{H}_5)_2$ and
   ii) $\text{Fe}\,(\text{CO})_3\,(\text{C}_8\text{H}_8)$

d) What is Negeshi coupling reaction? Explain with suitable example.

**Q3** Answer the following (any two) [10]

a) Explain the role of OMC's as protecting agent.

b) Discuss the role of metalloocene based catalyst for polymerization of propylene.

c) What is cativa process? Discuss its mechanism. How it is advantageous over Monsanto process.

d) Explain the catalytic role of alkyl molybdate (VI) Compounds in epoxidation reaction.

**Q4**

a) Write short note (any one) [5]

i) Metal complexes in asymmetric catalysis

ii) Organometallic compounds as electrophiles and nucleophiles.

b) Predict the product. [5]

i) $\text{Cp}\,(\text{CO})_3\text{Re} + \text{Br}_2 \rightarrow ?$

ii) $\text{Trans}\,(\text{PPh}_3)_2\text{Ir}\,(\text{CO})\text{Cl}H \rightarrow ?$

iii) $\text{Cis. Et. Re. (CO)}_5 + \text{CH}_3\text{CN} \rightarrow ?$

iv) $\text{Fe}\,(\text{COPh})\,(\text{CO})_2(\eta^5 - \text{C}_5\text{H}_5) \xrightarrow{hv} ?$

v) \text{Mn} + \text{Mn} \xrightarrow{hv} ?$

\[ \text{hv} \]

\[ \text{hv} \]
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[5123]-307
M.Sc. - II (Semester III)
INORGANIC CHEMISTRY
CHI - 330 : Inorganic Reaction Mechanism Photo Chemistry and Magnetic Properties of Coordination Compounds Chemistry
(2013 Pattern) (4 - Credit)

Time : 3 Hour]  

Instructions to the candidates:
1) All questions are compulsory.
2) Neat diagrams must be drawn wherever necessary.
3) Use of calculator is allowed.

Q1) Attempt the following [20]

a) Give the main types of inorganic reactions.

b) What is trans effect? Explain with suitable example.

c) Describe the phenomenon of fluorescence.

d) Name the various techniques used for studying fast reactions.

e) What do you mean by anation reaction? Give example.

f) List out the characteristics of inner - sphere electron transfer reactions

g) Explain the mechanism of isomerization reaction with suitable example.

h) Find out the R.S. term symbol for Mn$^{3+}$ and Ni$^{2+}$

i) Define the terms.

   i) Curie temperature

   ii) Ferromagnetism

P.T.O
j) Thermodynamically stable complexes could be kinetically inert or labile. Explain with suitable example.

**Q2** Answer the following (any two) [10]

a) What is SN1CB mechanism? Explain it with suitable example.

b) Discuss in detail the mechanistic steps involved in outer - sphere electron transfer reaction with suitable example.

c) Give an account of photo chemical reactions of Co (III) complexes.

d) Write a note on solute - solvent interactions.

**Q3** Answer the following (any two) [10]

a) Discuss the relationship between d electron configuration of the metal and lability of the complexes.

b) Give an account of insertion reactions.

c) Discuss in brief oxidative addition reaction.

d) The extent of exchange interaction in the Cu2 O2 ring system is greater than that in Cr2 O2 ring system. Explain.

**Q4** Answer the following [10]

a) Write a note on (any one)

i) Magnetic properties of mixed valence compounds.

ii) π - bonding theory.

b) Complete the following chemical equations.

i) \((CH_3)_3 B + N(CH_3)_3 \rightleftharpoons ?\)

ii) \(Cr(Co)_6 + Py \rightarrow ? + ?\)

iii) \([Fe (CN)_6]^{1-} + [Ir Cl_6]^{2-} \rightarrow ? + ?\)

iv) \(O_3S^{2-} + OCL^- \rightarrow ? + ?\)

v) \(BF_3 + F^- \rightarrow ?\)

\[\text{\textbullet} \text{\textbullet} \text{\textbullet}\]
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[5123]-308
M.Sc. -II
INORGANIC CHEMISTRY
CHI-331 : Physical Methods in Inorganic Chemistry
(2013 Pattern) (Credit System) (Semester-III)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) All questions are compulsory.
2) Draw neat diagrams wherever necessary.
3) Figures to the right indicate full marks.
4) Use of log tables and calculators is allowed.

Q1) Answer the following: [20]
   a) Define chemical shift.
   b) Write the a,b,c and $\alpha, \beta, \gamma$ for orthorhombic and monoclinic crystal system.
   c) Write the Bragg’s equation.
   d) Predict the number of lines expected in ESR spectra of NF$_3$ radical.
   e) Define the Isothermal, Quasistatic TGA.
   f) How will you calculate the ‘G’ factor in ESR?
   g) Draw the following planes in cubic cell [100], [111].
   h) Calculate the number of atom present in FCC lattice.
   i) Why DME used in cyclic voltammetry?
   j) Write the equation for calculating isomershift in Mössbauer spectroscopy.

Q2) Attempt any two of the following: [10]
   a) A cubic crystalline material of cell length 20.124 Å is to be examined by using Cu K$\alpha$ radiation ($\lambda = 1.542 Å$). At what angle would you expect to get the maximum reflection from the fourth order of (100) plane.
   b) Explain the use of cyclic voltammetry for detection of electrophilic reaction with suitable example.
   c) Discuss the ESR-Spectrum for naphthalene radical.
   d) Explain the Mössbauer spectra for the Fe(II) (phen)$_2$(NCS)$_2$.

P.T.O.
Q3) Attempt any two of the following: [10]
   a) Explain the factor’s affecting on DTA curve.
   b) Explain the principle, instrumentation of DSC.
   c) Calculate the % weight loss for CaC$_2$O$_4$·H$_2$O when heated in air at 3°C/min in platinum crucible.
   d) Write the reactions when Mn (pH$_2$O$_2$), H$_2$O heated at 5°C/min for their differential thermal analysis.

Q4) Attempt any two of the following: [10]
   a) Discuss the application of Mössbauer spectroscopy for the determination of nature of chemical bonding.
   b) Explain XPS is the surface analysis technique.
   c) Explain spin-lattice relaxation & anisotropic effect in ESR spectroscopy.
   d) Write short note on single crystal X-ray diffraction.
P1390

[5123]-309

M.Sc.-II

INORGANIC CHEMISTRY

CHI-332: Bioinorganic And Inorganic Medicinal Chemistry
(2013 Pattern) (Credit System) (Semester-III)

Time: 3 Hours]

Instructions to the candidates:
1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Draw neat diagrams wherever necessary.

Q1) Answer the following: [20]

a) Enlist the functions of blue copper proteins.

b) Why Mn^{2+} is biologically important? Mention oxidation states of manganese accessible in biology.

c) What are iron-sulfur proteins? Give any four biological conversions involving them.

d) What is super oxide dismutase? Explain its role in biological system.

e) Which element is present at the active centre of carboanhydrase? What is the function of carboanhydrase?

f) Define P-cluster & give its role.

g) Draw the structure of C_{u}-PSTM and C_{u}-ASTM.

h) What is the rate determining step in hydrolysis of CO_{2} by carboanhydrase.

i) What are Reiske proteins? Mention oxidation states at Fe centres.

j) Explain the structurally important components of MO containing enzymes.

Q2) Answer any two of the following: [10]

a) Write an account of Z_{n} containing enzymes.

b) Explain the following actions of alkyl cobalamin:
   i) One electron redox reaction.
   ii) C_{o}-C band cleavage.

c) Explain the mutase activity of coenzyme B_{12}.

d) Which metalloenzyme is responsible for removal of H_{2}O_{2}? Discuss its active site, structure and function.

P.T.O.
**Q3** Answer any two of the following: [10]

a) What is the oxidation state of vanadium in amavadin? Explain the structural features of amavadin.

b) Explain the role of $M_n$ in peroxidases.

c) Give an account of therapeutic and diagnostic applications of radiopharmaceuticals.

d) Give schematic diagrams of the following types of reactions

i) $O_2$ production at a four Manganese cluster.

ii) Biological Oxidation of phenylalanine in presence of Dopamine-$\beta$-mono oxygenase.

**Q4** Answer any two of the following: [10]

a) Write notes on:

i) MRI

ii) Antitumor agents.

b) Write a note on gamma scintigraphy and its applications.

c) Write notes on:

i) Galactose oxidase

ii) Ribonucleotide reductase.

d) Explain the mechanism of $C_{\text{u}}$-PSTM trapping inside cells.

☆ ☆ ☆
M.Sc. -II
ORGANIC CHEMISTRY
CH-O-350: Organic Reaction Mechanism
(2013 Pattern) (Semester - III)

Time : 3 Hours
[Max. Marks :50]

Instructions to the candidates:
1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Answer to the two sections should be written in separate answer books.

SECTION-I

Q1) Attempt any three of the following:

   a) Explain acylon condensation with suitable example.

   b) α-Phenyl ethyl cinnamate fail to undergo 1, 4 addition. Explain.

   c) Explain Riemer - Tiemann reaction with mechanism.

   d) Hydrolysis of \( \text{O} \text{N} \text{S} \text{CH}_2 \text{CH}_2 \text{C} \) is considerably slower than that of \( \text{CH}_2 \text{CH}_2 \text{Cl} \). Explain.

Q2) Write short notes on any two of the following:

   a) NGP by OAC group and \( \pi \) bond.

   b) Use of pyridoxal in reductive amination.

   c) Reactions of carbenes.

   d) Radical initiators and their functions.

P.T.O.
Q3) Predict the products for any four of the following: [8]

a) \[
\begin{align*}
\text{1, CH}_3\text{MgBr, CuCl} & \rightarrow \text{?} \\
\text{2. H}_2\text{O}\text{, }\text{H}^+ & \rightarrow \text{?}
\end{align*}
\]

b) \[
\begin{align*}
\text{CHCl}_3 & \rightarrow \text{?} \\
\text{NaOH} & \rightarrow \text{?}
\end{align*}
\]

c) \[
\begin{align*}
\text{PPA} & \rightarrow \text{?}
\end{align*}
\]

d) \[
\begin{align*}
\text{1, Me}_3\text{SiCl, Et}_3\text{N} & \rightarrow \text{?} \\
\text{2. }\text{Cl} & \rightarrow \text{?}
\end{align*}
\]

e) \[
\begin{align*}
\text{Ph-CH=CH}_2 & \rightarrow \text{?} \\
\text{CCl}_4, \text{hv} & \rightarrow \text{?}
\end{align*}
\]

SECTION-II

Q4) Explain any three of the following: [9]

a) Use of FAD and FADH\textsubscript{2} in biotransformation.

b) NGP by anil group with suitable example.

c) Claisen - Schmidt condensation.

d) Oxymercuration - demercuration with mechanism.

Q5) Suggest mechanism for any four of the following: [8]

a) \[
\begin{align*}
\text{Ph-H} & \rightarrow \text{?} \\
\text{80°C} & \rightarrow \text{?}
\end{align*}
\]

b) \[
\begin{align*}
\text{1, AIBN, Bu}_3\text{SnCl} & \rightarrow \text{?} \\
\text{NaBH}_3\text{CN} & \rightarrow \text{?}
\end{align*}
\]
Q6) Answer any two of the following: [8]

a) \[
\begin{align*}
\text{Me} & \quad - \quad \text{C} & \quad - \quad \text{C} & \quad - \quad \text{C} & \quad - \quad \text{C} & \quad - \quad \text{C} & \quad - \quad \text{Et} \\
\text{H} & \quad & & & & & \text{H}
\end{align*}
\]
decomposes on heating to give an ester in which \(\alpha\)-carbons in the alkyl and acyl groups retain configurations. Explain.

b) Triplet carbene add in non-stereospecific manner to olefins. Explain.

c) Explain the mechanism of racemization of amino acid using pyridoxal phosphate.
SECTION - I

Q1) Answer any four of the following:

a) \( \text{C}_3\text{H}_6\text{O}_2 \) shows two singlets of same intensities in its NMR at 2.3 & 4.0δ ppm. What is its probable structure.

b) A compound shows Mt at 84 and base peak at 56 its PMR shows single peak at 1.4δ ppm. Assign the correct structure.

c) A compound with a molecular formula \( \text{C}_6\text{H}_8 \) shows only two signals in its \( ^{13}\text{C} \)-NMR. DEPT shows presence of CH & CH\(_2\) assign probable structure.

d) Arrange the following compounds in decreasing order of Jvicinal. Justify your order.

\[
\begin{align*}
\text{H}_a & \quad \text{H}_a \\
\text{H}_b & \quad \text{H}_b \\
\text{C}_3 & \quad \text{C}_3 \\
\text{H}_q & \quad \text{H}_q
\end{align*}
\]

and

\[
\begin{align*}
\text{H}_a & \quad \text{H}_a \\
\text{H}_b & \quad \text{H}_b \\
\text{C}_3 & \quad \text{C}_3 \\
\text{H}_q & \quad \text{H}_q
\end{align*}
\]

e) Distinguish the following Pairs by indicated spectroscopic methods.

a) \[
\begin{align*}
\text{H}_a & \quad \text{H}_a \\
\text{H}_b & \quad \text{H}_b \\
\text{C}_3 & \quad \text{C}_3 \\
\text{H}_q & \quad \text{H}_q
\end{align*}
\]

by \( \text{MS} \)

b) \[
\begin{align*}
\text{H}_a & \quad \text{H}_a \\
\text{H}_b & \quad \text{H}_b \\
\text{C}_3 & \quad \text{C}_3 \\
\text{H}_q & \quad \text{H}_q
\end{align*}
\]

by \( ^{13}\text{C} \)-NMR
Q2) Answer any three of the following:

a) \( \text{C}_7\text{H}_{14}\text{O} \) has two isomeric ketones whose PMR and CMR Signals are shown below assign the structures to each of the ketones from data provided.

i) PMR : 1.2 d (12 mm), 28(septet, 2mm)  
CMR : 18 (str), 38(m), 214(w)  
ii) PMR : 1.0 s(9mm) 2.2 s(3mm) 2.31 (2mm)  
CMR : 30(str), 32(w), 34(w), 56(m) 210(w).

b) A compound \( \text{C}_6\text{H}_{10}\text{O}_2 \) exhibits the following spectral data. Analyse the signals and arrive at a consistent structure. Justify your assignment.

CMR : 12(q); 13(q); 22(t); 127(s); 147(d) 174(s)  
 PMR : 1.17 t 7.5Hz 3H; 1.85d, 1.5Hz 3H; 2.2(dq. 7.5 & 6.3Hz 2H; 6.9, tq 1.5 & 6.3Hz 1H; 12.7 bs 1H

c) A compound with M+ 100 shows the following spectral data. Analyse the data systematically arrive at a structure based on your analysis.

MS(M/z) : 100, 85, 71, 56, 44 ↔  
CMR : 13(q); 20(t); 32(t); 68(t); 86(t); 152(d)  
PMR : 1.0 t 7 Hz gmm; 14 m 6mm; 1.6 m 5.8 mm; 3.7 t 7Hz 6 mm  
4.0 dd 9 & 2Hz 3 mm; 4.1 dd 13 & 2Hz 3 mm 6.5 dd 13 & 9 Hz 3 mm  
Cosy : 6.5 ↔ 4.0, 4.1  
1.0 1.4  
1.4 1.0, 1.6  
1.6 1.4, 3.7  
4.0 6.5  
4.1 4.0
d) A compound with MF C$_{10}$H$_{12}$O$_2$ shows the following spectral data analyse data and arrive at a structure consistant with the data

CMR : 146; 144; 137, 132; 121. 2; 115.5; 114; 111; 56; 40
PMR : 3.3 bd 7Hz 2H; 3.87 S 3H; 4.52 bd 1H exchangeable; 5.03 ddt 17.2 & 1.2 Hz 1H; 5.15 ddt 9.7,2 & 1.2 Hz 1H; 5.95 ddt 17, 9.7 & 6.8 Hz 6.61 dd 8& 2 Hz 1H; 6.68 d 2Hz 1H; 6.85 d 8Hz 1H.
NOE : Irritate at 6.68 → 3.32 & 3.87 line intensities increase.

e) Assign the structure to the compound with MF C$_{9}$H$_{16}$O$_2$
IR : 1740 cm$^{-1}$
PMR : 0.9 (t, 7.6 Hz 3H); 1.3 (M, 4H); 1.65 (m.2H); 2.32(t 6.7 Hz 2H); 4.58 (d,7.8Hz, 2H); 5.21(d, 10.4Hz 1H); 5.32(d,15.9Hz 1H); 5.92 (ddt 7.8, 10.4 & 15.9 Hz 1H).
CMR : 13.9(q); 22.3(t); 24.7(t) 31.3(t); 34.2(t); 64.9(t); 118(t); 132(d) and 174(s)

Q3) Assign the signals to various protons in compound A. Use decoupling data for the confirmations of the assignments justify your assignments. [5]

Irradiation Experiments:

a) Irradiation at 2.97 changes 2.70(t) to singlet          1.4 2 S, 3H; 1.95 t 6Hz 2H; 2.55 s 3H; 2.7 t 6 Hz 2H; 2.82 d 6Hz 3H; 2.92 s 1H; 4.12 s 1H; 5.33q 6Hz 1H; 6.37d, 8Hz, 1H; 6.78 dd, 2Hz 1H; 6.87 dd, 8 & 2Hz 1H.
b) Irradiation at 2.82 changes 5.33(q) to singlet

c) Irradiation at 6.87 changes 6.37(d) & 6.78 (d) to singlet.
SECTION - II

**Q4)** Write the short notes on any three.

a) Use of lanthanide shift reagents.

b) Spin decoupling techniques.

c) Factors affecting germinal coupling.

d) Double focusing technique in MS.

e) Use of DEPT & Off. resonance decoupling techniques in CMR.

**Q5)** Answer any four of the following.

a) Explain the genesis of ions in the following compounds

\[ \text{a)} \quad \text{b) } \]

\[ \begin{array}{c}
198, 196, 169, 167, 103
\end{array} \]

\[ \begin{array}{c}
56, 41
\end{array} \]

b) Explain in brief a working of electron impact mass spectrometry.

c) Differentiate the following compounds by MS

\[ \begin{array}{c}
\text{OCH}_3 \\
\text{CO}_2\text{H}
\end{array} \]

d) An amine C\textsubscript{7}H\textsubscript{15}N shows the following ions in MS. Deduce probable structure

M/e: 84(100%); 70, 56, 113, 98, 85

e) Explain the techniques used to arrive at the molecular formula in MS.

**Q6)** The spectra of all unknown compound are shown on the adjacent page. Analyse the spectra and use to arrive at a correct structure of the unknown. Justify your assignment.
C, 36.5%; H, 10.0%

No UV maximum above 200 nm

$\log(\varepsilon/\lambda)$

$\delta$  
$\delta'$  
$\delta''$  
$\delta'''$

$C_9H_{13}O_2Br$  
$196/198$

$\delta$  
$\delta'$  
$\delta''$

$400$ MHz in CDC$_3$

$\delta$  
$\delta'$  
$\delta''$

$\delta$  
$\delta'$  
$\delta''$

$\delta$  
$\delta'$  
$\delta''$

Proton noise decoupled
M.Sc.
ORGANIC CHEMISTRY
CHO - 352 : Organic Stereochemistry
(2013 Pattern) (Semester - III)

Time : 3 Hours
Max. Marks : 50

Instructions to the candidates:
1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Answers to the two sections should be written in separate answer book.

SECTION - I

Q1) Answer any four of the following:

a) Explain the difference of reactivities for solvolysis of cis and trans - 4 - t - butyl cyclohexyl tosylate with the help of energy profile diagram.

b) β-keto acid (A) is highly resistant to decarboxylation, explain.

\[ \text{(A)} \]

\[ \text{COOH} \]

c) Discuss the structure and stability of cis and trans \( g \) - methyl decalins.

d) Draw conformational structures of the compound I and II. Give their nomenclature and discuss the stability.

\[ \text{(I)} \]

\[ \text{(II)} \]

e) Reaction of cyclohexene with performic acid followed by hydrolysis gives trans - 1,2-diol, whereas similar reaction of trans cyclodecene gives trans 1,6-diol.

P.T.O.
Q2) Predict the product/s in any four of the following and explain stereochemical principles involved. Justify.

a)

\[ \text{NaOEt} \]

b)

\[ \text{H}_2 \text{Catalyst} \]

c)

d)

\[ \text{Base} \]

e)

\[ \text{BBr}_2 \]

Q3) a) Write the correct IUPAC names for the following compounds.

i)

ii)

iii)
b) Write short notes on any two of the following: 

i) Von Auwers - Skita Rule

ii) Anomeric effects

iii) I strain

SECTION - II

Q4) Answer any three of the following:

a) Write applications of plain rotatory dispersion curves.

b) Describe the properties of good resolving agent.

c) Trans stilbene shows high absorption in uv spectra than cis stilbene.

d) Explain how will you determine the configuration in geometrical isomers of o-hydroxy cinnamic acid.

Q5) Answer any four of the following:

a) Explain the term positive cotton effect.

b) Describe briefly racemic solid solution.

c) Explain the role of menthyl amine as a resolving agent.

d) Cis - stilbene on hydroxylation with $\text{kM}_n \text{O}_4$ gives meso diol and trans stilbene gives dl pair of diol.

e) What is the product obtained from the reduction of (2s, 3r) - 2,3 - dichloro cyclo butanone with LiAlH$_4$ by attack from the Re side?
Q6) a) Predict the product/s in any two of the following and explain stereochemical principles involved. Justify. [4]

i) \[
\begin{align*}
\text{Cyclopropane} & \xrightarrow{\text{Ph}_3\text{P} = \text{Cu Li}} \text{Et}_2\text{O} \\
\circ & \text{to} \ 20^\circ\text{C} \quad ? \\
\end{align*}
\]

ii) \[
\begin{align*}
\text{Ph-C-H} & \xrightarrow{\text{NBS}} \text{H}_2\text{O} \\
\circ & \text{m} \text{SO} \quad ? \\
\end{align*}
\]

iii) \[
\begin{align*}
\text{Ph-} & \text{H} \\
\text{C-H} & \xrightarrow{\text{cat. TSOH}} \text{ACOH} \\
\circ & \text{75}^\circ\text{C} \quad ? \\
\end{align*}
\]

Syn alcohol

b) How would you determine the stereochemistry of compound A and B using NMR. [4]

![Chemical structures](image)

\[\times \ 	imes \ 	imes\]
[5123] - 313
M.Sc. -II
ORGANIC CHEMISTRY
CHO-353: Photochemistry, Pericyclic Reactions and Heterocyclic Chemistry
(2013 Pattern) (Semester - III)

Time : 3 Hours] [Max. Marks :50
Instructions to the candidates:
1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Answers to the two sections should be written in separate answer book.

SECTION-I

Q1) Explain the following (all sub questions are compulsory): [10]

a) Cyclobutanone undergoes three type of photo reactions.

b) [1, 3] sigmatropic shift of hydrogen is thermally forbidden but photochemically allowed.

c) Irradiation of benzene yields a mixture of three products.

\[ \text{Cyclobutane} \xrightarrow{\text{166 - 220nm}} \text{Product 1} + \text{Product 2} + \text{Product 3} \]

d) Explain the thermal ring opening of cis-3, 4 - dimethyl cyclobutene.

e) Complete the following reaction.

\[ \text{Cyclobutene} \xrightarrow{\text{Vapour phase}} \text{Product} \]
Q2) Answer the following (Any two):

a) i) Construct a correlation diagram for the conrotatory process for the inter conversion of cyclohexadiene $\xleftarrow{}$ Hexatriene system. Whether the process is thermally or photochemically allowed.

ii) $\xrightarrow{\text{hu}}$ Predict the product/s and mechanism for above reaction.

b) i) Complete the following reaction

ii) $\xrightarrow{\text{hu}}$ Predict the product/s and suggest the mechanism.

c) i) Complete the following sequence of reaction

ii) $\xrightarrow{\text{hu}}$ $\xrightarrow{\text{H}^+}$ Ph $\xrightarrow{}$ CH = CH$_2$ + CH$_2$N$_2$ $\xrightarrow{\Delta}$
d) i) Predict the product/s with suitable mechanism

\[ \text{350}^\circ \text{C} \]

ii)

Q3) Write notes on any Two: [5]

a) Photochemical reactions in isocomene.

b) Paterno - Butchi reaction.

c) Photorearrangement of 4, 4- disubstituted 2, 5 - cyclohexadienones.

SECTION-II

Q4) Answer all the questions in brief: [10]

a) Pyrazole has a higher boiling point than its N-alkyl derivative.

b) Why glycerol is used and not directly acrolein is used in skraup Quinoline synthesis.

c) Pyrrole - 2 - carbaldehyde does not take part in benzoin or Perkin condensation while furfural does.

d) The diazines are more resistant to electrophilic attack than pyridine.

e) Explain how Coumarin is converted in to benzofuran.

Q5) Do as directed Any two of the following: [10]

a) How following conversion could be achieved.
b) Identify A, B, C, D from the following

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{Li(Hg)}} \text{A} & \xrightarrow{\text{HCl}} & \text{B} & \xrightarrow{\text{H}_2/\text{Ni}} & \text{C} \\
& & \downarrow & \downarrow & \downarrow & \downarrow \\
& & & \text{D} & & \\
\end{align*}
\]

c) What is the reaction of phenyl magnesium bromide with pyrimidine followed by treatment with dilute acid and then reacting the product with KMnO₄ in Acetone. Suggest the mechanism for the following conversions.

d) [Chemical structures and reactions]

Q6) Write a note on any one of the following:

a) Bischler indole synthesis.

b) Pictet - Spengler synthesis.

c) Skraup quinoline synthesis.
P1395

[5123]-314

M.Sc. - II

ANALYTICAL CHEMISTRY

CHA-390: Electroanalytical and Radioanalytical Methods of Analysis (2013 Pattern) (Credit System) (Semester-III)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic table, non programmable calculator is allowed.

SECTION -I

Q1) Answer the following: [10]

a) State any two applications of amperometry.

b) State and explain Faraday’s second law of electrolysis.

c) Explain the following terms:
   i) Limiting current.
   ii) Residual current.

d) State two applications of hydrodynamic voltammetry.

e) Give disadvantages of dropping mercury electrode.

Q2) Attempt any two of the following: [10]

a) Distinguish between differential pulse polarography and square-wave polarography.

b) Explain the criteria of reversibility of electrochemical reactions.

c) Explain the principle of amperometric titrations. Draw and discuss nature of amperometric titration curve when an electroactive reagent added into an electroinactive solution.

P.T.O.
d) An electroactive species yielded a wave with limiting current of 15.2\(\mu\)A at a rotating disk electrode which was rotated at 10 r/s. What limiting current would be expected at 30 r/s?

**Q3)** Attempt any one of the following: 

a) What are applications of coulometric titrations? List the advantages and limitations of coulometric titrations.

b) A sample of copper ore weighing 3.325 g is dissolved in acid and the copper is electrolysed using constant current of 2.5 A for 7.5 min. Calculate the percentage of copper in ore.

[Given: At. Wt. of Cu = 63.54]

**SECTION - II**

**Q4)** Answer the following: 

a) State applications of radiometric titration.

b) Distinguish between DTA and DSC.

c) Give the applications of neutron activation analysis.

d) Explain the following terms:

i) Flux.

ii) Saturation activity.

e) Explain the principle of inverse isotope dilution analysis.

**Q5)** Attempt any two of the following: 

a) Discuss the principle and technique of radiometric titrations. Draw and describe the nature of radiometric titration curve when only titrant is radioactive.

b) Explain, How to determine the volume of blood in patient by isotope dilution analysis?

c) Describe with suitable examples the effect of particle size of the sample, heating rate and furnace atmosphere on the nature of TGA curve.
d) An ancient gold coin weighing 3.5g was irradiated for 5 hours in neutron flux of $10^7$ n cm$^{-2}$ s$^{-1}$ and activity of $^{198}$Au formed, having $t\frac{1}{2} = 64.373$ hours measured immediately after irradiation was found to be $5 \times 10^3$ counts per sec. The neutron absorption cross-section of $^{197}$Au is 98.8 barns. Calculate percentage purity of gold coin.

**Q6)** Attempt any one of the following: [5]

a) Explain the principle of thermometric titrations. Describe the nature of thermometric titration curve for exothermic and endothermic reactions.

b) Calculate the percentage of MgCO$_3$ and CaCO$_3$ in 65 mg of limestone sample that exhibits thermogram showing weight of 56 mg at 500°C and 36 mg at 900°C.

[Given: At. Wt. of Ca = 40.08, Mg = 24.31, C = 12, O = 15.99]
M.Sc. II
ANALYTICAL CHEMISTRY
CHA-391: Pharmaceutical Analysis
(2013 Pattern) (Credit System) (Semester - III)

Time: 3 Hours
Max. Marks : 50

Instructions to the candidates:
1) Answer to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic table, non-programmable calculator is allowed.

SECTION - I

Q1) Answer the following: [10]
   a) What is sterilization? Name different methods of sterilization.
   b) Write the principle involved in microbial assay by turbidimetric method.
   c) Differentiate drugs and cosmetics.
   d) What are limit tests? Give their importance.
   e) What is stability of drug?

Q2) Attempt any two of the following: [10]
   a) Describe in detail biological assay of tetanus antitoxin.
   b) Explain in detail ‘Disintegration test’ for capsules
   c) Explain “control of pharmaceutical industries by FDA”.
   d) Describe the limit test for iron and sulphate.

Q3) Attempt any one of the following: [5]
   a) Describe in detail ‘determination of moisture content from pharmaceutical preparation’.
   b) Write a note on ‘protolytic activity’.

P.T.O.
SECTION-II

Q4) Answer the following: [10]
   a) Give advantages of emulsions.
   b) Differentiate between tablet and capsules.
   c) Define Aerosols: Give its classifications.
   d) What are good storage conditions for pharmaceutical product?
   e) How sulphated ash in vegetable drug is determined?

Q5) Attempt any two of the following: [10]
   a) What are solutions in pharmaceutical preparations; Explain aqeous type of solution in detail.
   b) Explain in detail microbial and cross contamination.
   c) Give an assay of ‘isoniazide’.
   d) 0.2g of aspirin \((C_9H_8O_4)\) sample was dissolved in 25ml distilled water to which 10ml (0.5m) sodium hydroxide solution was added and mixture was boiled in water bath for 20 minutes, on cooling the solution was titrated with 0.5m HCL. The Burette reading was 5.5ml. The blank titration reading was 9.9ml Determine the percentage of Aspirin in a given sample.

Q6) Attempt any one of the following: [5]
   a) What are ophthalmic preparation? Give its classification.
   b) 0.5g of ferrous fumarate tablet \((C4H_2FeO_4)\) was dissolved in 15ml dil \(H_2SO_4\) by gentle heating and diluted to 100ml. 10ml of this solution was titrated against 0.25N ceric ammonium sulphate. It gave burette reading of 8.2ml. Calculate % of ferrous fumarate in given tablet.

\[\text{[Given } C=12; \text{ H}=1; \text{ O}=16; \text{ Fe}=56]\]
Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic table/ non programmable calculator is allowed.

SECTION-I

Q1) Answer the following questions: [10]
   a) Give the principle of liquid-liquid extraction.
   b) What are the advantages and limitations of solid phase extraction?
   c) Explain preservation of organic compound on SPME fibre.
   d) What is the effect of microwave on sample?
   e) Why modifiers are added in SFE?

Q2) Attempt any two of the following. [10]
   a) Draw a schematic diagram of SPE system. Explain it’s essential components.
   b) Explain purge and Trap techniques for volatile organic in aqueous system.
   c) Outline the experimental procedure for solid phase micro extraction. Give it’s applications.
   d) Explain heating effect of microwave in MAE.

Q3) Attempt any one of the following: [5]
   a) Give the experimental procedure for SPME. Give it’s applications.
   b) Drawn schematic diagram of MAE device and explain its essential components.

P.T.O.
SECTION-II

Q4) Attempt the following: [10]
   a) What is LASER?
   b) State two applications of ICPMS.
   c) Explain the mechanism of Hallow cathod lamp.
   d) What is counter electrode?
   e) Explain the spectral interference in AAS.

Q5) Attempt any two of the following: [10]
   a) Enlist the different types of mass analyzer. Explain any one of them in detail with diagram.
   b) What is micronutrients? Explain the estimation of copper from soil sample.
   c) State the principle of AFS. Explain its instrumentation with diagram.
   d) Write a short note on
      i) RIS and
      ii) DCP

Q6) Solve any one of the following: [5]
   a) The calcium was analyzed by FES, the standard solution of calcium (3.00 μg/ml) gives meter reading 62.3 at 422.7nm. The analyte gives meter reading 36.4 at 422.7nm. Calculate the amount of calcium in analyte.
   b) The mass spectrum of nitrogen produced air is characterized by the presence of peaks of isotopic forms of nitrogen $^{14}$N $^{15}$N and $^{14}$N $^{15}$N equal to 362 and 33mm respectively what is the % of nitrogen $^{15}$N in the sample?
P1398

[5123]-317

M.Sc.-II

ANALYTICAL CHEMISTRY

CHA-380: I- Analytical Method Development and Validation
II- Geochemical and Alloy Analysis
III- Laboratory Automation and Sensor Based Techniques
(2013 Pattern) (Credit System) (Semester-III)

Time : 3 Hours

Max. Marks : 50

Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic table, non programmable calculator is allowed.

SECTION-I

Q1) Answer the following:

a) Define: Absolute error and Gross error.
b) How to estimate reliability of result.
c) Explain standard deviation.
d) What is method modification and revalidation?
e) Give five topics which are selected for Initial Harmonization.

Q2) Attempt any two of the following:

a) Enlist essential principle of method transfer. Explain any two of them.
b) Describe inter-laboratory qualification process.
c) Explain the term: Specificity and selectivity.
d) Consider following set of data:

<table>
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<tr>
<th></th>
<th>Set A</th>
<th>Set B</th>
<th>Set C</th>
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</thead>
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<td>True obs.</td>
<td>True</td>
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<td>38.803</td>
</tr>
<tr>
<td>0.0716</td>
<td></td>
<td>38.85</td>
<td></td>
</tr>
</tbody>
</table>

Find absolute error in the measurement.

P.T.O.
Q3) Attempt any one of the following: 

a) Explain United State Pharmacopia and national formulary. 

b) If fluorescence intensity of test solution containing quinine was 16.10. The following values have been determined: 
\[ \sum x_i=1.00 \quad \sum y_i= 49.5, \quad \sum x_i^2 = 0.30 \]
\[ \sum x_i^2 = 1.000 \quad \sum x_i y_i = 14.73 \]
The number of points (n=5), Calculate independent variable (x in μg/ml) by linear regression method.

SECTION-II
( Geochemical and Alloy Analysis )

Q4) Answer the following: 

a) How organic carbon of soil is determined? 

b) What is composition of solder and steel alloy? 

c) Give the principle for estimation of copper from bronze alloy. 

d) What is sampling? Give the method for sampling of soil. 

e) Enlist any two ores of iron. Give their minor constituents. 

Q5) Attempt any two of the following: 

a) Discuss in brief procedure for estimation of total potassium from soil. 

b) Give the procedure for estimation of calcium and magnesium from dolomite ore. 

c) Outline the method for determination of chromium from steel. 

d) 0.310g of organic compound analyzed for its Nitrogen content by Kjeldahl’s method. The evolved ammonia was absorbed in 50ml of 0.11 N HCl. The remaining HCl was back titerated with 0.11 N NaOH gives burette reading of 21.2 ml. Calculate the percentage of Nitrogen in given sample.

Q6) Attempt any one of the following: 

a) Write a note on cation exchange capacity of soil. 

b) 2.6 gm of Bronze alloy was dissolved in 5 ml conc.HNO₃ and diluted to 250 ml. A 50 ml aliquot of this solution is mixed with 20 ml of 1% benzoic oxine solution to precipitate copper as copper-oxine complex. The resultant complex on drying and heating give precipitate of CuO which is found to weigh 0.423 gm. Calculate the percentage of copper in given sample. 

[Given At. Wt Cu= 63.54g 0=16g]
SECTION-III

(Laboratory Automation and Sensor Based Techniques)

Q7) Answer the following: [10]
   a) What is flow injection Analyzer?
   b) State any four achievements of bio transduction.
   c) What is microfabrication?
   d) Enlist different types of analyzers.
   e) What is automatic titrations?

Q8) Attempt any two of the following: [10]
   a) Explain serial and parallel integration.
   b) Discuss in detail chemical sensors.
   c) Explain continuous flow analyzer.
   d) Write a note on cylindrical robot.

Q9) Attempt any one of the following: [5]
   a) Explain surface acoustic wave sensor.
   b) Write a note on piezoelectric quartz crystal resonator.
M.Sc.

PHYSICAL CHEMISTRY

CHP - 410 : Molecular Structure and Spectroscopy
(2013 Pattern) (Semester - IV) (New)

Time : 3 Hours

Instructions to the candidates:

1) All questions are compulsory.
2) Answers to the two sections should be written in separate answer books.
3) Neat diagrams must be drawn wherever necessary.
4) Figures to the right side indicate full marks.
5) Use of logarithmic tables / calculator is allowed.

Physico-Chemical Constants

1. Avogadro Number
   \( N = 6.022 \times 10^{23} \text{ mol}^{-1} \)
2. Boltzmann Constant
   \( k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} \)
   \( = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \)
3. Planck Constant
   \( h = 6.626 \times 10^{-27} \text{ erg s} \)
   \( = 6.626 \times 10^{-24} \text{ J s} \)
4. Electronic Charge
   \( e = 4.803 \times 10^{-10} \text{ esu} \)
   \( = 1.602 \times 10^{-19} \text{ C} \)
5. 1 eV
   \( = 23.06 \text{ k cal mol}^{-1} \)
   \( = 1.602 \times 10^{-12} \text{ erg} \)
   \( = 1.602 \times 10^{-19} \text{ J} \)
   \( = 8065.5 \text{ cm}^{-1} \)
6. Gas Constant
   \( R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} \)
   \( = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
   \( = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \)
7. Faraday Constant
   \( F = 96487 \text{ C equiv}^{-1} \)
8. Speed of light
   \( c = 2.997 \times 10^{10} \text{ cm s}^{-1} \)
   \( = 2.997 \times 10^{8} \text{ m s}^{-1} \)
   \( = 4.184 \times 10^{7} \text{ erg} \)
   \( = 4.184 \text{ J} \)
9. 1 cal
   \( = 4.184 \times 10^{7} \text{ erg} \)
10. 1 amu
    \( = 1.673 \times 10^{-27} \text{ kg} \)
11. Bohr magneton
    \( \beta_e = -9.274 \times 10^{-24} \text{ J T}^{-1} \)
12. Nuclear magneton
    \( \beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1} \)
13. Mass of an electron
    \( m_e = 9.11 \times 10^{-31} \text{ Kg} \)

P.T.O.
SECTION - I

Q1) Attempt the following: [10]
   a) What is spin decoupling?
   b) Explain the advantages of TMS.
   c) Give significance of g-value.
   d) What is the concept of electric field gradient?
   e) How are X-rays produced?

Q2) Attempt any two of the following: [10]
   a) Explain Larmor precession. What is Larmor Frequency?
   b) Describe the instrumentation used in nqr spectroscopy with a suitable diagram.
   c) Define diffraction and give a brief account of any one method for investigating the structure of crystals.
   d) Discuss zero field splitting in esr.

Q3) Solve any one of the following: [5]
   a) Calculate the radio frequency of absorption for a free electron, if a magnetic field of strength 340 mT is applied.
   b) Calculate the nmr frequency of $^{35}$Cl in a magnetic field of intensity 1.8 T.

SECTION - II

Q4) Answer precisely the following: [10]
   a) Define the terms - Diffraction and X-ray diffraction.
   b) Write Van Vleck’s equation for magnetic susceptibility and explain the terms therein.
   c) What are the limitations of electron diffraction technique?
   d) Enlist the counter methods used to detect x-rays.
   e) What are the advantages of faraday method over the Gouy method?
Q5) Answer any two of the following: [10]
   a) Write a note on diamagnetism and paramagnetism.
   b) Discuss the identification of unit cell from systematic absences in diffraction pattern.
   c) Discuss the applications of electron diffraction technique.
   d) Explain the differences between neutron diffraction and x-ray diffraction.

Q6) Solve any one of the following: [5]
   a) Using Pascal’s constants and constitutive corrections given below, calculate the molar susceptibilities of benzoate ion (C7H5O2-) Pascal’s Constants in cgs unit: C = – 6.00 × 10⁻⁶
      H = – 2.93 × 10⁻⁶
      Constitutive correction: C in ring = –0.24 × 10⁻⁶.
   b) The density of lysozyme crystals was 1.240 gL⁻¹. The crystals contained only 52% protein. Calculate the mass of dry protein per unit cell.

   [Given : The unit cell dimensions of lysozyme crystal in Å are 79.78.8 and 37.9]

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PHYSICAL CHEMISTRY

CHP - 411 : Surface Chemistry and Electrochemistry
(2013 Pattern) (Semester - IV) (New)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) All questions are compulsory.
2) Answers to the two sections should be written in separate answer books.
3) Neat diagrams must be drawn wherever necessary.
4) Figures to the right side indicate full marks.
5) Use of logarithmic table/calculator is allowed.

### Physico - Chemical Constants

<table>
<thead>
<tr>
<th>1) Avogadro Number</th>
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<td>4) Electronic Charge</td>
<td>( e = 4.803 \times 10^{-10} \text{ esu} = 1.602 \times 10^{-19} \text{ C} )</td>
</tr>
<tr>
<td>5) 1 eV</td>
<td>( = 23.06 \text{ k cal mol}^{-1} = 1.602 \times 10^{-12} \text{ erg} = 1.602 \times 10^{-19} \text{ J} = 8065.5 \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>6) Gas Constant</td>
<td>( R = 8.314 \times 10^{7} \text{ ergK}^{-1} \text{ mol}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>7) Faraday Constant</td>
<td>( F = 96487 \text{ C equiv}^{-1} )</td>
</tr>
<tr>
<td>8) Speed of light</td>
<td>( c = 2.997 \times 10^{10} \text{ cm s}^{-1} = 2.997 \times 10^{8} \text{ m s}^{-1} )</td>
</tr>
<tr>
<td>9) 1 cal</td>
<td>( = 4.184 \times 10^{7} \text{ erg} = 4.184 \text{ J} )</td>
</tr>
<tr>
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<td>( = 1.673 \times 10^{-27} \text{ kg} )</td>
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<td>11) Bohr magneton</td>
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<td>12) Nuclear magneton</td>
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<tr>
<td>13) Mass of an electron</td>
<td>( m_e = 9.11 \times 10^{-31} \text{ kg} )</td>
</tr>
</tbody>
</table>

P.T.O.
SECTION - 1

Q1) Answer precisely the following: [10]

   a) Enlist the types of adsorption depending upon the types of phases in contact.

   b) Draw and explain the physical adsorption isotherm II.

   c) Write the relationship between adorption and surface tension and define the terms in it.

   d) Define condensed film. Give its equation.

   e) What is capillary condensation? Write the Kelvin’s equation.

Q2) Answer any two of the following: [10]

   a) Starting with chemical potential, derive the equation for isosteric heat of adsorption.

   b) Discuss the potential theory of multilayer adsorption.

   c) Explain the factors affecting the detergent action.


Q3) Solve any one of the following: [5]

   a) The adsorption of butane on NiO powder was measured at 0°C, the volumes of butane at STP adsorbed per gram of NiO are

      | P/kPa | 7.543 | 11.852 | 16.448 | 20.260 | 22.959 |
      | V/(cm³/g) | 16.46 | 20.72  | 24.38  | 27.13  | 29.08  |

      Using Langmuir isotherm, calculate the volume at STP per gram when the powder is covered by a monolayer.

   b) The surface tensions of dilute solutions of phenol in water at 30°C were:

      | wt% phenol | 0.024 | 0.047 | 0.118 | 0.471 |
      | γ, dynes cm⁻¹ | 72.6  | 72.2  | 71.3  | 66.5  |

      Calculate ‘γ’ from the Gibbs equation for a 0.1% solution.
SECTION - II

Q4) Answer Precisely the following:

a) Define ionics and electrodics.
b) Enlist the methods of corrosion prevention.
c) Explain the ways of transport of ions.
d) Write the overall cell reaction for charging and discharging of lead acid accumulator.
e) Write the reactions taking place in electrochemical reduction of ketones.

Q5) Answer any two of the following:

a) Define the terms:
   i) Outer potential
   ii) Surface potential
   iii) Galvani potential and
   iv) Electrochemical potential
b) Derive Tafel equation using Butler-Volmer equation.
c) Write a note on $H_2-O_2$ fuel cell.
d) Deduce the equation for thickness of ionic atmosphere.

Q6) Solve any one of the following:

a) Evaluate the constants A and B for ethyl alcohol at 25°C. Hence calculate mean activity coefficient of $KNO_3$ in ethyl alcohol at 25°C when ionic strength is 0.05.

   [Given: Dielectric constant of ethyl alcohol = 24.3, Ion size parameter $a = 3\, \text{Å}$]

b) The exchange current density at $pt[H_2(g)]H^+_{(aq)}$ electrode at 278 K is 0.79 mAm$^{-2}$. How much current flows through the standard electrode having total surface are 5 cm$^2$ when the overvoltage is 5 mV. [Given: $\beta = 0.5$]
M.Sc.

PHYSICAL CHEMISTRY

CHP - 412 : Materials Chemistry and Catalysis
(2013 Pattern) (Semester - IV) (New)

Time : 3 Hours]  
[Max. Marks : 50

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic table/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1) Avogadro Number  \( N = 6.022 \times 10^{23} \text{ mol}^{-1} \)

2) Boltzmann Constant  \( k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ mole}^{-1} \)
   \( = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ mole}^{-1} \)

3) Planck Constant  \( h = 6.626 \times 10^{-27} \text{ erg s} \)
   \( = 6.626 \times 10^{-44} \text{ J s} \)

4) Electronic Charge  \( e = 4.803 \times 10^{-10} \text{ esu} \)
   \( = 1.602 \times 10^{-19} \text{ C} \)

5) 1 eV
   \( = 23.06 \text{ kcal mol}^{-1} \)
   \( = 1.602 \times 10^{-12} \text{ erg} \)
   \( = 1.602 \times 10^{-19} \text{ J} \)
   \( = 8065.5 \text{ cm}^{-1} \)

6) Gas Constant  \( R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} \)
   \( = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
   \( = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \)

7) Faraday Constant  \( F = 96487 \text{ C equiv}^{-1} \)

8) Speed of light  \( c = 2.997 \times 10^{10} \text{ cm s}^{-1} \)
   \( = 2.997 \times 10^{8} \text{ m s}^{-1} \)
   \( = 4.184 \times 10^{7} \text{ erg} \)
   \( = 4.184 \text{ J} \)

9) 1 cal
   \( = 1.673 \times 10^{-27} \text{ kg} \)

10) 1 amu

11) Bohr magneton  \( \beta_e = -9.274 \times 10^{-24} \text{ J T}^{-1} \)

12) Nuclear magneton  \( \beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1} \)

13) Mass of an electron  \( m_e = 9.11 \times 10^{-31} \text{ kg} \)

P.T.O.
SECTION - I

Q1) Attempt the following: [10]
   a) State two advantages of hi-tech materials.
   b) What is Langmuir-Blodgett film?
   c) What is sputtering? Give its types.
   d) Explain types of rectifiers.
   e) How does doping affect critical temperature?

Q2) Attempt any two of the following: [10]
   a) Discuss the structure of 1-2-3 superconductors.
   b) Describe low dimensional quantum structures of IV - V compounds.
   c) Explain the superconductivity in cuprates.
   d) What is N-P-N transistor? Explain the three modes of its operation.

Q3) Attempt any one of the following: [5]
   a) A light bulb with carbon filament has 200Ω resistance. The power supply has zero resistance. Find filament temperature [Temperature coefficient of resistivity for carbon is $-5 \times 10^{-4}$ C$^{-1}$ at $t_0 = 20^\circ$C] 
   b) 89% light passes through a 20cm thick solid. Find the absorption coefficient.

SECTION - II

Q4) Attempt the following: [10]
   a) Define the terms functionality and ‘poisoning’.
   b) How is a catalyst industrially useful?
   c) Give the properties of zeolites.
   d) Define ‘catalyst selectivity’.
   e) Enlist the steps in Langmuir - Hinshelwood mechanism.
Q5) Attempt any two of the following: [10]
   a) Discuss the role of catalysts in green chemistry.
   b) Describe the sol-gel method for preparing catalysts.
   c) Discuss the mechanism of chemisorption.
   d) Write a note on auto-exhaust catalyst.

Q6) Attempt any one of the following: [5]
   a) The adsorption of a gas on tungsten surface follows the Langmuir isotherm
      with $K = 0.45 \text{kPa}^{-1}$. Calculate the equilibrium pressure when the fractional
      surface coverage is 0.15.
   b) CO is adsorbed on charcoal at 273K. From the data given find the
      Langmuir constant $K$ and volume for complete coverage.

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<tr>
<th>P/kPa</th>
<th>V/cm(^3)</th>
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<td>66.7</td>
<td>36.9</td>
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<td>80</td>
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M.Sc.

PHYSICAL CHEMISTRY

CHP - 413 : Biophysical Chemistry
(2013 Pattern) (Semester - IV) (New)

Time : 3 Hours

Instructions to the candidates:
1) Answers to the TWO sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic table/calcualtor is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1) Avogadro Number \( \text{N} = 6.022 \times 10^{23} \text{ mol}^{-1} \)
2) Boltzmann Constant \( k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \)
3) Planck Constant \( h = 6.626 \times 10^{-27} \text{ erg s} = 6.626 \times 10^{-24} \text{ J s} \)
4) Electronic Charge \( e = 4.803 \times 10^{-10} \text{ esu} \)
5) \( 1 \text{ eV} = 23.06 \text{ kcal mol}^{-1} \)
\( = 1.602 \times 10^{-12} \text{ erg} \)
\( = 1.602 \times 10^{-19} \text{ J} \)
\( = 8.065 \times 10^{-1} \text{ cm}^{-1} \)
6) Gas Constant \( R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} \)
\( = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
\( = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \)
7) Faraday Constant \( F = 96487 \text{ C equiv}^{-1} \)
8) Speed of light \( c = 2.997 \times 10^{10} \text{ cm s}^{-1} \)
\( = 2.997 \times 10^{8} \text{ m s}^{-1} \)
9) \( 1 \text{ cal} = 4.184 \times 10^{7} \text{ erg} \)
\( = 4.184 \text{ J} \)
10) \( \text{I amu} = 1.673 \times 10^{-27} \text{ kg} \)
11) Bohr magneton \( \beta_{e} = -9.274 \times 10^{-24} \text{ J T}^{-1} \)
12) Nuclear magneton \( \beta_{n} = 5.051 \times 10^{-27} \text{ J T}^{-1} \)
13) Mass of an electron \( m_{e} = 9.11 \times 10^{-31} \text{ kg} \)
SECTION - I

Q1) Attempt the following: [10]
a) Define proteins and classify them.
b) How do biological energy processes obey first and second laws of thermodynamics?
c) Write and explain Bragg’s equation.
d) Enlist types of biological reactions.
e) What is gel electrophoresis?

Q2) Attempt any two of the following: [10]
a) Explain the structure and functions of proteins.
b) Discuss the classification of RNA.
c) What is electrophoresis? Explain its types.
d) State the principle of XRD. How is applied to study the molecular weight of an asymmetric macromolecule.

Q3) Attempt any one of the following: [5]
a) Discuss the reactions involved in ATP hydrolysis.
b) Calculate the standard free energy of the reaction Dihydroxy acetone phosphate catalyst glyceraldehyde 3 phosphate. At equilibrium, the ratio of the product to reactant is 0.0475 at 7pH and 25°C.

SECTION - II

Q4) Answer precisely the following: [10]
a) Mention three layers of a cell membrane with dimensions.
b) Define the terms - Axolemna and endocytosis.
c) How is the size of biopolymer particles, determined by Brownian motion method?
d) What is uncompetitive enzyme inhibition?
e) Define - Circular dichroism (CD).
**Q5** Attempt any two of the following: 

a) Discuss the mechanism of muscle contraction.

b) Describe the end-group determination method to determine the molecular weight of a biopolymer.

c) Derive the Michaeli’s - menton equation for enzyme catalysis.

d) Discuss the application of circular dichroism to study the conformation of biomolecules.

**Q6** Attempt any one of the following: 

a) Fractions of a biopolymer, when dissolved in an organic solvent, gave the following intrinsic viscosities at 25°C.

<table>
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<tr>
<th>M (g mol⁻¹)</th>
<th>34,000</th>
<th>61,000</th>
<th>1,30,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>[η]</td>
<td>1.02</td>
<td>1.6</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Determine K and α in Mark-Hounrink equation.

b) A biopolymer sample has the following distribution of molecular weight.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>0.15</th>
<th>0.20</th>
<th>0.40</th>
<th>0.15</th>
<th>0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol wt</td>
<td>1 × 10⁴</td>
<td>1.5 × 10⁴</td>
<td>2 × 10⁴</td>
<td>3 × 10⁴</td>
<td>4 × 10⁴</td>
</tr>
</tbody>
</table>

Calculate $\bar{M}_n$ and $\bar{M}_w$. 

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M.Sc.

PHYSICAL CHEMISTRY

CHP - 414 : Special Topics in Nuclear and Radiation Chemistry
(2013 Pattern) (New) (Semester - IV)

Time : 3 Hours]
[Max. Marks : 50

Instructions to the candidates:

1) Answers to the TWO sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic table/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1) Avogadro Number
\[ N = 6.022 \times 10^{23} \text{ mol}^{-1} \]
2) Boltzmann Constant
\[ k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} \]
\[ = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \]
3) Planck Constant
\[ h = 6.626 \times 10^{-27} \text{ erg s} \]
\[ = 6.626 \times 10^{-24} \text{ J s} \]
4) Electronic Charge
\[ e = 4.803 \times 10^{-10} \text{ esu} \]
\[ = 1.602 \times 10^{-19} \text{ C} \]
5) 1 eV
\[ = 23.06 \text{ kcal mol}^{-1} \]
\[ = 1.602 \times 10^{-12} \text{ erg} \]
\[ = 1.602 \times 10^{-19} \text{ J} \]
\[ = 8065.5 \text{ cm}^{-1} \]
6) Gas Constant
\[ R = 8.314 \times 10^{2} \text{ ergK}^{-1} \text{ mol}^{-1} \]
\[ = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \]
7) Faraday Constant
\[ F = 96487 \text{ C equiv}^{-1} \]
8) Speed of light
\[ c = 2.997 \times 10^{10} \text{ cm s}^{-1} \]
\[ = 2.997 \times 10^{8} \text{ m s}^{-1} \]
9) 1 cal
\[ = 4.184 \times 10^{7} \text{ erg} \]
\[ = 4.184 \text{ J} \]
10) 1 amu
\[ = 1.673 \times 10^{-27} \text{ kg} \]
11) Bohr magneton
\[ \beta_e = -9.274 \times 10^{-24} \text{ J T}^{-1} \]
12) Nuclear magneton
\[ \beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1} \]
13) Mass of an electron
\[ m_e = 9.11 \times 10^{-31} \text{ kg} \]
SECTION - I

**Q1** Attempt the following: [10]

a) Give an account of inelastic scattering.

b) Discuss the working of Quartz Fibre electrometer.

c) Describe with suitable example Szilard-Chalmer’s reaction.

d) Draw and explain Vande Graff generator.

e) Explain the principle of Radioimmuno assay technique.

**Q2** Attempt any two of the following: [10]

a) Derive Breit Wigner formula.

b) Which points are to be considered while applying MPD values?

c) Explain the principle of Positron emission somography technique.

d) What were the reasons for chernobyl accident? Write after effects of this accident.

**Q3** Solve any one of the following: [5]

a) Find out the excitation energy of a compound nucleus formed by bombarding $^{27}$Al with 8MeV $\alpha$-particles. Given: Atomic mass & $^{27}$Al = 26.981535, $\alpha$=4.002604, $^{31}$P = 30.973763 amu.

b) Find out the dose due to 500mli CS - 137 source at a distance of 5 meters. Given: $E_v = 0.667$MeV.

SECTION - II

**Q4** Attempt the following: [10]

a) Give AERB guidelines for classification of solid waste.

b) Write the reactions in radiolysis of alkanes.

c) What is solar neutrino problem?

d) Draw a schematic diagram of experimental set-up for studying radiometric titrations based on complex formation.

e) What is pulse radiolysis?
**Q5)** Attempt any two of the following: [10]

a) Draw and explain C-N-O bicycle.

b) Write a note on neutralization radiometric titration.

c) Write a note on management of medium level liquid radioactive waste.

d) Discuss the effect of solute concentration on Molecular yield.

**Q6)** Solve any one of the following: [5]

a) 25mL of K*Cl was titrated with 0.01 M AgNO₃ radiometrically. Addition of 2mL of AgNO₃ showed loss in activity from 24000 counts/4min to 2000 counts/5min. Find the amount of KCl if background counts are 50 counts/5min.

[Given : At wt. K = 39.1, Cl = 35.5]

b) Find the thickness of pb required to reduce the activity from 25000 cpm to 15000 cpm.

[Given: \( \mu_e = 0.211 \text{ b/e}^- \), Z = 82, A = 207, density = 11.35 g/cm³.]
INORGANIC CHEMISTRY
CHI-430: Inorganic Polymers and Heterogeneous Catalysis
(2013 Pattern) (Semester-IV) (4-Credit)

Time : 3 Hours

Instructions to the candidates:
1) All questions are compulsory.
2) Neat and labeled diagram must be drawn wherever necessary.
3) Figures to the right indicate full marks.

Q1) Answer the following questions: [20]
   a) Catalytic poisons are not always bad. Explain with suitable example.
   b) Differentiate between chemisorption and Physisorption.
   c) What are the advantages of bimetallic catalyst over the monometallic counter part?
   d) What do you mean by porous material? Give their Classification.
   e) Draw a flow sheet diagram for the synthesis of ZSM-S.
   f) How Roney-Nickel catalyst is prepared? Write down the chemical reaction involved in the process.
   g) What do you mean by intercalated and pillered clays?
   h) What are perovskites? Give at least two examples of use of perovskite oxide as a oxidation catalyst.
   i) Draw the structure of (S₄N₅)
   j) Explain the difference between polymolybdate and polytungstate.

Q2) Answer any two of the following: [10]
   a) What is chemical reactor? Give their types. Explain construction, working and types of fixed bed reactors.
   b) Discuss in detail the characteristics of zeolite framework structure.
   c) Give an account of use of zeolite as a hydrocracking catalyst.
   d) Describe about various postsynthetic treatment given to heterogeneous catalysts.

P.T.O
Q3) Attempt the following (Any Two): [10]
   a) Discuss the role of bismuth molybdate in the oxidation and ammoxidation of propylene.
   b) Give an account of surface characterization methods used for characterization of heterogeneous catalyst.
   c) Explain various methods of immobilisation of transition metal complexes.
   d) Discuss the use of heteropolyanions as a catalyst.

Q4) Write a short note (Any two) [10]
   a) Use of semiconducting oxide as a Photocatalyst.
   b) MFI & MEL type zeolites.
   c) Industrial applications of heterogeneous catalysts.
   d) Phosphonitrilic Polymers.

⭐ ⭐ ⭐
INORGANIC CHEMISTRY
CHI-431: Material Science-I
(Solid State & Other Inorganic Materials)
(2013 Pattern) (Semester-IV) (New 4-Credits)

Time : 3 Hours]                      [Max. Marks : 50
Instructions to the candidates:
1) All questions are compulsory.
2) Neat and labelled diagrams must be drawn wherever necessary.
3) Figures to the right indicate full marks.

Q1) Answer the following questions: [20]
   a) What is line defect? Explain its types.
   b) What is dimagnetism? Explain with suitable example.
   c) What are Spinels? Explain their types.
   d) What is effect of temperature on magnetic susceptibility value of ferromagnetic materials? Explain with graphical representation.
   e) Explain the synthesis of super conductors.
   f) Explain the applications of super conducting materials.
   g) A piece of wood containing moisture weighed 75.5 gm. and after over drying showed constant weight is 60.1 gm. Calculate the moisture content.
   h) How ceramic materials are classified?
   i) Give classification of Biomaterials.
   j) Explain the hydration process of cement.

Q2) Attempt any two of the following: [10]
   a) What is diffusion? Explain the different types of diffusion mechanisms.
   b) What is Hysteresis loop? Explain with remanent magnetisation and coercive force.
   c) Explain Cardiovascular and dental applications of biomaterials.
   d) Explain different types of Portland cement.
Q3) Attempt any two of the following: [10]

a) Explain the different applications of magnetic materials.

b) Discuss BCS theory of Superconductors.

c) Explain Meissner effect. What are type I and type II Superconductors?

d) The saturation magnetisation of BCC iron is 1750 KA/m. Calculate the net magnetic moment per iron atom in BCC.
   (Given: Lattice parameter = 2.87 Å)

Q4) Write short notes on (Any two): [10]

a) Piezoelectric materials.

b) Macrostructure of wood.

c) Asphalt.

d) i) Macroldefect free cement.
   ii) Oil-well cement.

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INORGANIC CHEMISTRY

CHI - 432 : Material Science - II (Nanomaterials)
(2014 Pattern) (Semester - IV) (4 Credits)

Time : 3 Hours  [Max. Marks : 50]

Instructions to the candidates:
1) All questions are compulsory.
2) All questions carry equal marks.
3) Use of calculators is allowed.

Q1) Answer the following: [20]

a) What do you mean by quantum wire, quantum sheet & quantum dot?

b) Why cavitation occurs in the synthesis of nanoparticles?

c) What is a carbon nanotube? How the carbon nanotubes are differentiated as zigzag, armchair and chiral nanotube.

d) Explain the formation of mesoporous nanomaterials.

e) Define piezoelectricity and pyroelectricity.

f) Why nanoparticles shows high electrical conductivity?

g) Explain the targeted drug delivery mechanism using suitable example.

h) How silver nanoparticles are prepared? Give the chemical reaction involved in it.

i) Write about sonochemical method for preparation of nanoparticles.

j) What are rectifiers?

Q2) Answer the following (any Two): [10]

a) What is nanotechnology? Name the various methods for synthesis of nanoparticles. How these methods are important?

b) How semiconductors are prepared using nanomaterials?

c) Discuss the chemical reduction method for the synthesis of Fe-Cu bimetallic nanoparticle.

d) How Raman spectroscopy is useful in characteristic nanoparticles?
Q3) Answer the following (any two):  

a) Explain the principle, construction and working of transmission electron microscope.

b) Explain how thermocouple operates on the basis of principle of Peltier and seeback effect.

c) Explain how spectroscopy is useful in characterization of nanoparticles.

d) What are nanosensors? Explain their different types.

Q4) Answer the following (any two):

a) What is diode? Explain the working of p-n-junction diode with the help of bond energy diagram.

b) What is nano-composite material? Explain any Four size dependent properties of nanomaterials.

c) What are nanoporous materials? Explain the synthesis methods for nanoporous materials.

d) Explain the preparation of pbse nanowire by solvothermal method.
INORGANIC CHEMISTRY

CHI - 445 : Inorganic Chemistry; Applications in Industry,
Environment and Medicine
(2013 Pattern) (Semester - IV)

Time : 3 Hours
Instructions to the candidates:
1) Attempt any two sections of the following.
2) Both sections should be written in the same answer book.
3) All questions are compulsory.
4) Figures to the right indicates full marks.
5) Neat diagram must be drawn wherever necessary.
6) Use of logarithmic table / calculator is allowed.

SECTION - I
Applications in Industry

Q1) Answer the following: [10]
   a) What is meant by natural or mineral pigments?
   b) What is meant by “Acid Bath”? Where is it used?
   c) Explain the use of chromium in dyeing of wool using azo dyes.
   d) What are the different processes available for electro deposition of zinc?
   e) Give, preparation and physical properties of Lithopone.

Q2) Answer the following: (any two) [10]
   a) What are formazans? How are they classified as ligands? Give at least two examples of each and draw the structure of metal complexes they form.
   b) Explain the methods for electroplating of precious metals.
   c) Give two examples and draw structures of
      i) Metallized dyes
      ii) Additional reagents, and
      iii) Medially metallized azodyes.
      iv) How do complexes such as prussian blue and Ferrocene modify the behaviour of electrodes during electroplating?
Q3) Write a note on any one:
   a) Alloy plating.
   b) Blue and Yellow pigment.
   c) Metal complexes of azo dyes.

SECTION - II

Environment

Q4) Answer the following:
   a) List the five provision of the clear water act. (CWA).
   b) What is powerball? How is the powerball manufactured?
   c) Draw a schematic diagram of a moleten carbonate fuel cell. (MCFC). Write the reaction that occur at the cathode and anode.
   d) List the best option for energy sources for 21st century.
   e) What is the EPA maximum permissible level of the following metals, in drinking water?
      i) Lead
      ii) Arsenic
      iii) Cadmium
      iv) Mercury

Q5) Answer the following any two:
   a) Draw a schematic diagram that shows all of the component of an atomic absorption spectrometer (AAS). The Metal ion analyte has a positive charge, how does it become a neutral atom?
   b) What is meant by point and nonpoint sources of pollution? Give an example of each.
   c) The COD is a measure of what type of pollutant in water? Describe how you do a COD test on a water sample.
   d) Mercury (Hg^{2+}) has a t½ of 8 days. If a person injects 3mg/day. Calculate the steady state concentration of mercury.
Q6) Write a note on any one:
   a) Energy from Biomass.
   b) Water and Tidal Power.
   c) Industrial waste treatment.

SECTION - III
Applications of Metal Ions in Medicine

Q7) Attempt the following:
   a) What are the modes of binding of Bismuth complexes to biomolecules?
   b) What is the significance of vanadium phosphate relation in living organism?
   c) What are chemotherapeutic drugs? Give two examples.
   d) What are chemical nucleases? What is their functions? Give one example.
   e) Which are the drugs used in treatment of Rheumatoid arthritis?

Q8) Answer any two:
   a) Discuss the non-associative interactions of metal complexes with DNA.
   b) Explain the therapeutic role of Lithium.
   c) “Gold complexes show anticancer activity”. Explain.

Q9) Write short note on (any one):
   a) Cryotherapy.
   b) Biomedical use of Lithium.
Q1) Outline the steps involved in the following synthetic sequence. Indicate the reagent used and discuss the mechanism and stereo chemistry involved. [10]
Q2) Answer the following (any two):

a) Give chemical and physical evidence to prove presence of \( \text{\texttt{C = C}} \) group in Hardwickiic acid.

b) Give evidence to prove
i) The presence of –OH group in comptothecin.
ii) The presence of lactone ring.

c) Explain the behaviour of Rodophyclotoxin acetate and epipodo phyllo toxin acetate towards pyrolysis.

Q3) Answer the following (Any one).

a) Write a note on cyclotrimerization reaction.

b) Discuss the evidence to establish the presence of C5 methyl group in Hardwickiic acid.

SECTION - II

Q4) Suggest biogenesis for the following.

a) GPP →

b) 

c) \(^{13}\text{CH}_3\text{COSCOA} \rightarrow \text{GGPP. Indicate the position of labelled carbons.}\)

d) \(\text{NH}_2(\text{CH}_2)_4\text{CH NH}_2\text{COOH} \rightarrow\)

e) 

[5123]-410
Q5) Answer the following (any two).

a) Outline the steps involved in the following conversion.

\[
\text{CHO} \quad \text{Oglu} + \text{Trypto phen} \rightarrow \text{Product}
\]

b) 2Z, 6E FPP → 

c) Squalene monolpoxide →

Q6) Attempt any one of the following:

a) Write a note on importance of wagner meerwin shift in biogenesis of terpenoids.

b) Give the biogenetic steps involved in the following conversion:

\[
\text{MeO} \quad \text{CHO} \quad \text{LOH} \rightarrow \text{Product}
\]
SECTION - I

Q1) Predict the product/s of the following: [10]

a) \[
\begin{align*}
\text{PhCO} & \quad \text{Me} \\
\text{PhCH}_2 & \quad \text{HMe}
\end{align*}
\]
\[
\text{Cl}_2\text{TiCl}_2 + \text{AlMe}_3 \quad \text{pyridine}
\]

b) \[
\begin{align*}
\text{OEt} & \quad \text{H}_2, \text{Pd-BINAP-Ru} \\
\text{OEt} & \quad \text{CH}_3\text{COOH, DEAD, PPh}_3
\end{align*}
\]

c) \[
\begin{align*}
\text{Me} & \quad \text{NaOEt, MeOH} \\
\text{Ph} & \quad \text{PhCOOEt, H}^+
\end{align*}
\]

d) \[
\begin{align*}
\text{I} & \quad \text{Pd(PPh}_3)_4, \text{CO, 1,4-dioxane} \\
\text{OEt} & \quad \text{Me}_3\text{Si}
\end{align*}
\]

e) \[
\begin{align*}
\text{CO} & \quad \text{PdH}_2/\text{PdCl}_2(PPh}_3)_2 \\
\text{PPh}_3\text{CNCOOEt/Ph-H}
\end{align*}
\]

P.T.O.
Q2) Suggest the mechanism in any four of the following:

a) 

\[
\text{Ar} + \text{H} \xrightarrow{\text{N-CH}_2\text{Ph}} \text{ArCH} = \text{CH}_2 + \text{Cl} \xrightarrow{\text{NaH, LiCl, CH}_2\text{Cl, Trityl}} \text{ArCH} = \text{CCH}_2\text{Cl} \xrightarrow{\text{pyridine}} \text{ArCH} = \text{CH}_2 \text{Cl}
\]

b) 

\[
\text{H}_2 \xrightarrow{\text{HCl(OC)O}} \text{ArCH}_2\text{CH}_2\text{OCH} = \text{CH}_2 \xrightarrow{\text{pd (PPh}_3)_4} \text{ArCH}_2\text{CH}_2\text{OCH} = \text{CH}_2
\]

c) 

\[
\text{C_6H}_5 \xrightarrow{\text{Pd (PPh}_3)_4} \text{ArCH} = \text{CH} = \text{CH}_2
\]

d) 

\[
\text{H}_8\text{C}_6 \xrightarrow{\Delta} \text{ArCH} = \text{CH}_2 \xrightarrow{\text{pd (PPh}_3)_4} \text{ArCH} = \text{CH}_2
\]

e) 

\[
\text{ArN} = \text{N} \xrightarrow{\text{ArNH}_2, \text{THF}} \text{ArNH}_2
\]

Q3) Answer in any two of the following:

a) Write a note on Kumada Coupling.

b) Application of Reppe reaction.

c) Explain with mechanism Julia Lythgoe Olefination.
SECTION - II

Q4) Predict the product/s of the following:

a) \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\xrightarrow{\Delta} \\
\xrightarrow{(i)} \text{CHD} \\
n
\]

b) \[
\begin{array}{c}
\text{Ph} \\
\text{CHO}
\end{array}
\xrightarrow{\text{Ph} \xrightarrow{\text{N}_3} \text{N}_3} \\
\xrightarrow{\text{92}, 18 \text{ hr}}
\]

c) \[
\begin{array}{c}
\text{CHO} \\
\text{C}
\end{array}
\xrightarrow{\text{BH}_2} \\
\xrightarrow{\text{i) CO, H}_2, \text{ Pressure} \text{ high}} \\
\xrightarrow{\text{ii) H}_2\text{O}_2, \text{NaOH}}
\]

d) \[
\begin{array}{c}
\text{CHO} \\
\text{C}
\end{array}
\xrightarrow{\text{BH}_2} \\
\xrightarrow{\text{i) CO, H}_2, \text{ Pressure} \text{ high}} \\
\xrightarrow{\text{ii) H}_2\text{O}_2, \text{NaOH}}
\]

[5123]-411
Q5) Suggest the Mechanism in any four of the following: [10]

a) \[ \text{Ph} - CH_3 + \text{PhH}_3,\text{DEAD} \rightarrow \text{Ph} - \overset{\text{O}}{\text{CH}_3} \]

b) \[ \text{PhCOOH} \rightarrow \text{PhCH}_2\text{OH} \]

c) \[ \text{G} - \overset{\text{O}}{\text{OE}_2} \]

d) \[ \text{Ph} - CH_3 + \text{CN} \rightarrow \text{Ph} - CH_2\text{CN} \]

e) \[ \text{Me} - \overset{\text{O}}{\text{Bn}} \]

Q6) Answer in any two of the following: [5]

a) Write a note on Pauson-Khand reaction.

b) Discuss the role of chiral organoboranes in Organic Synthesis.

c) Use of g-BBN in organic synthesis.
M.Sc.

ORGANIC CHEMISTRY

CHO - 452 : Carbohydrate, Chiron Approach, Chiral Drugs and Medicinal Chemistry

(New Course) (2013 Pattern) (Semester - IV)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Answers to the two sections should be written in separate answer book.

SECTION - I

Q1) Answer any Five of the following:

a) Explain the term Chiron and Chiron pool strategy. [2]

b) Give the reagent for the following conversion. [2]

\[
\begin{align*}
\text{CHO} & \xrightarrow{?} \text{CHO} & \xrightarrow{?} \text{CHO} & \xrightarrow{?} \text{CHO}
\end{align*}
\]

\[
\begin{align*}
\text{CHO} & \xrightarrow{?} \text{CHO} & \xrightarrow{?} \text{CHO} & \xrightarrow{?} \text{CHO}
\end{align*}
\]

c) Give the retro synthesis of (−) Pentanomycin. [2]

d) Give the product & explain Mechanism in above reaction. [2]

\[
\begin{align*}
\text{CHO} & \xrightarrow{\text{BzNHCH}_2} \text{CHO} & \xrightarrow{\text{H}_2\text{O, }\text{NaNH}_2} \text{CHO}
\end{align*}
\]

e) Complete the following reaction. [2]

(Write reagents & product in each step)

\[
\begin{align*}
\text{CHO} & \xrightarrow{?} \text{CHO} & \xrightarrow{?} \text{CHO} & \xrightarrow{?} \text{CHO}
\end{align*}
\]

f) Give the synthesis of L(−) alanine from 2-amino-2-deoxy-D-Glucose. [2]

P.T.O.
Q2) Answer the following (Any Five):  
   a) What are the distomers? Explain the distomers with side effects and with no side effects.  
   b) Give the pharmacological activity of S-Ibuprofen.  
   c) What are Chiral drugs? What is the need of Chiral drugs? How Chirality enhance pharmacological activity?  
   d) Give the medical uses and side effects of indinavir.  
   e) Give the synthesis of Griseofulrin.  
   f) Give the reactions of D-Glucose with (Any two):  
      i) \(\text{HNO}_3\)  
      ii) \(\text{Br}_2\)-water  
      iii) \(\text{HCN}\)

Q3) Answer the following questions (Any two):  
   a) How can oxidation with \(\text{HNO}_3\) be used to distinguish between D-erythrose and D-threose?  
   OR  
   a) Why do aldohexose give positive Fehling and osazone reactions but negative schift and bisulfite test?  
   b) Write short note on “Anomeric effect”.  
   c) Show how D-Glucose is converted to \(\alpha,\beta\) - D-Glucopyranose and \(\alpha,\beta\)-D-Gluco furanose.

SECTION - II

Q4) Solve Any 5:  
   a) Give an brief account of Mode of action of Quinolones.  
   b) What are general characteristics desired for the antibiotics.  
   c) Discuss SAR of Chloramphenicol.  
   d) Explain the term selective toxicity with an example.  
   e) What are tetracyclins.  
   f) Explain the various types of bonding involved in Drug-Receptor interactions.
**Q5** Solve Any 2: [10]

a) i) Give a brief account of Antifungal Agents.
   ii) Explain the Mode of action of Sulphonamides.

b) i) Give a brief account of Antiviral Agents.
   ii) Explain the term Antimetabolites with an example.

c) i) Write note on: Enzymes as Drug targets.
   ii) Discuss the drugs acting as inhibitors of protein synthesis.

**Q6** Solve any 1: [5]

a) Discuss the structural differences of Bacterial and fungal cells with respect to Animal Cell. Also explain how these differences help in selective toxicity of antibiotics.

b) What are β-lactum antibiotics? Discuss the strategies used to modify penicillin - g to achieve its oral absorption & acid stability. Also explain its mode of action.
P1410

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M.Sc. - II

ORGANIC CHEMISTRY

CHO - 453 : Designing Organic Synthesis and Asymmetric Synthesis (2013 Pattern) (Semester - IV)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:

1) All questions are compulsory.
2) Figures to the right indicate full marks.
3) Answers to the two sections should be written in separate answer books.

SECTION - I

Q1) Answer the following: [10]

a) Urethane protection of amino group is better than the amide protection in Peptide Synthesis. Explain.

b) Explain the uses of nitroalkanes in Organic Synthesis.

c) THP ethers are preferred over Methylene ethers in the protection of hydroxyl group. Justify.

d) Give the Synthetic equivalents to the following Synthons.

\[ \begin{align*}
\text{COOH} & , \\
\text{C}_6\text{H}_5\text{CO} & 
\end{align*} \]

e) Cyanohydrin is an effective method for umpolung of reactivity at aldehyde carbonyl. Explain.

P.T.O.
Q2) a) How will you effect the following conversions? [any two] [5]

i) \[ \text{Ph} \xrightarrow{\text{OCH}_3} \xrightarrow{\text{OBN}} \]

ii) \[ \text{CONH}_2 \xrightarrow{} \]

iii) \[ \text{CH}_3\text{CHO} \xrightarrow{} \xrightarrow{\text{OEt}} \]

b) Predict the products in any two of the following: [5]

i) \[ \text{Si-O-} \xrightarrow{\text{Cl}_3} \xrightarrow{\text{Bu}_4\text{NF}} \xrightarrow{\text{H}_2\text{O}} \]

ii) \[ \text{Me}_2\text{CuLi} \xrightarrow{\text{ether}} \xrightarrow{\text{CH}_3\text{I}} \]

iii) \[ \text{Ph} \xrightarrow{\text{NBS}} \xrightarrow{\text{MeOH, ether}} \xrightarrow{\text{CO}_2} \]

Q3) a) Using retrosynthetic analysis, suggest suitable method to synthesise any one of the following: [3]

i) \[ \text{COCH}_3 \]

ii) \[ \text{Ph} \]

[5123]-413
b) Arrange the given reagents in proper order to accomplish following conversion. Write the structures of the intermediates.

\[ \text{A} \quad \text{O} \quad \text{C} \quad \text{OH} \quad \xrightarrow{\text{K}_2\text{CO}_3, \text{MeOH; MeLi, ether; PCC, CH}_2\text{Cl}_2; \text{nBu}_4\text{NF, THF; TBDMSCl, Py, DMF.}} \quad \text{CH}_3 \quad \text{H} \quad \text{O} \quad \text{OH} \]

**SECTION - II**

**Q4** Complete the following conversions and suggest the correct stereochemistry of the product/s with the help of mechanism (All Sub questions are compulsory).

\[ \begin{align*}
\text{a) } & \quad \text{R, } \text{BOC} \\
1. \text{Li, EtNH}_2 & \quad \xrightarrow{2. \text{m-CPBA}} \\
\text{b) } & \quad \text{PhCHO + R-N} \\
\text{Et}_2\text{CO} & \quad \xrightarrow{\text{i Pr}_2\text{NET}} \\
\text{c) } & \quad \text{Ph} \quad \text{CHO} \\
30 \text{ psi } \text{H}_2 & \quad \xrightarrow{\text{Rh(I)}-\text{Ligand}} \\
\text{d) } & \quad \text{Ph} \quad \text{Ph} \\
1. \text{OsO}_4 & \quad \xrightarrow{-78^\circ\text{C}} \\
2. \text{NaHSO}_3 & \quad \\
\text{e) } & \quad \text{O} \\
1. \text{SAMP} & \quad \xrightarrow{2. \text{LDA}} \quad \xrightarrow{3. \text{CH}_2\text{H}_5\text{I}} \\
\end{align*} \]
Q5) Answer any two of the following: [10]

a) Justify the following observations with suitable reagents and stereochemical model.

\[ \begin{align*}
\text{i)} & \quad \text{Ph}_{3}PCH=CH_{2} \xrightarrow{?} \text{Ph}_{2}POCH=CH_{2} \\
\text{ii)} & \quad \text{NH}_{2}CH_{2}CO_{2}H \xrightarrow{?} \text{CH}_{3}CO_{2}H
\end{align*} \]

b) Define the following terms:

i) Houk model.

ii) Chiral organoboranes.

c) Comment on the following statements and justify it with an appropriate examples.

i) “Stereoselective epoxidation can also be carried out without allylic hydroxyl group”.

ii) Monosaccharide are referred as Chiral pool.

d) Complete the following conversions and comment on the optical purity.

\[ \begin{align*}
\text{i)} & \quad \text{}\xrightarrow{?} \quad \text{Catalyst} \quad \text{THF} 0^\circ \text{C} \\
\text{ii)} & \quad \text{}\xrightarrow{?} \quad \text{Catalyst} \quad \text{THF} 0^\circ \text{C} \\
\text{iii)} & \quad \text{}\xrightarrow{?} \quad \text{Catalyst} \\
\end{align*} \]
Q6) Complete the following multistep asymmetric synthesis using appropriate reagents on intermediates (Any one):

\[ \text{(5) - proline} \xrightarrow{\text{Br} \text{OCOCl}} \text{N} \text{aOH} \xrightarrow{\text{H}_2\text{O}} \text{MeOH/H}^+ \xrightarrow{\text{PhMeCl}} (2 \text{eq}) \xrightarrow{1. \text{HCl}} \xrightarrow{2. \text{NaOH}} \xrightarrow{3. \text{MeC}(\text{OH})_2} \]

\[ \text{a) } \text{Ti} \text{(Dipp)4} \xrightarrow{\text{BuOH}} \text{EtO} \xrightarrow{\text{K}_2\text{CO}_3} \text{NaH} \xrightarrow{\text{AcBr}} \xrightarrow{\text{K}_3\text{Fe(CC} \text{CN})_6} \text{DHQD} \text{D} \text{PHAL} \xrightarrow{\text{EtOH}, \text{Base}} \]

\[ \text{b) } \text{norephedrine} \xrightarrow{\text{EtO}} \xrightarrow{\text{K}_2\text{CO}_3} \text{NaH} \xrightarrow{\text{AcBr}} \xrightarrow{\text{K}_2\text{CO}_3, \text{MeOH}} \xrightarrow{\text{DHQD} \text{D} \text{PHAL}} \text{EtOH}, \text{Base} \]
P1411

[5123]-414

M.Sc.-II

ANALYTICAL CHEMISTRY

CHA-481: Analytical Toxicology and Food Analysis

(2013 Pattern) (Semester-IV)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:

1) Answer to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic tables/non programmable calculator is allowed.

SECTION-I

Q1) Answer the following: [10]

a) Give classification of coma.

b) Give the principle and identification of amphetamine and methamphetamine type C procedure.

c) Define the terms:
   i) Opium
   ii) Addict

d) Give the principle of isolation and identification of cocaine and heroin.

e) Explain ‘Narcotics’.

Q2) Attempt any two of the following: [10]

a) How barbiturates are isolated? Explain its procedure type C in detail.

b) Write a note on “Illicit traffic”.

c) Outline the procedure for determination of benzodiazepines.

d) How heroin is isolated from urine sample? Give detail procedure for its absorption and elution.

P.T.O.
**Q3** Attempt any one of the following: [5]

a) Explain color test of poison.

b) Urine sample is analysed for caffeine content by gas chromatographic method. It gave following results:
   i) Concentration of caffeine in reference standard=25mg/ml.
   ii) Peak height of caffeine in sample=57 min.
   iii) Peak height of caffeine in reference standard=82 min.

Calculate the concentration of caffeine in given sample.

**SECTION-II**

**Q4** Answer the following: [10]

a) What are sweetening tablets? Give it’s types.

b) What are carbohydrates? Give the classification of carbohydrates.

c) Explain procedure for determination of oil from oil seeds.

d) How pasteurization of milk is verified?

e) Discuss the method used for the estimation of iodine value of oil.

**Q5** Answer any two of the following: [10]

a) Explain method for estimation of benzoic acid from food sample.

b) Discuss the steps involved in identification of coal-tar dye present in food stuff.

c) Give the principle and outline the method for estimation of protein by Lowry’s method.

d) Describe a method for determination of 4-hydroxybenzoate.
Q6) Answer any one of the following:

a) When 20.0 ml milk requires for neutralization of 3.2 ml of 0.1N Na0H. Calculate amount of lactic acid in milk sample.

[Given: Molecular weight of lactic acid : 90]

b) Biological sample was determined for net protein utilization, digestibility and biological value gives following result.

i) Intake nitrogen (I)=18.1 mg.

ii) Faecal nitrogen (F)=8.1 mg.

iii) Endogenous faecal nitrogen (F_ε)=5.1 mg.

iv) Urinary nitrogen (u)=9.1 mg.

v) Endogenous urinary nitrogen (U_ε)=4.3 mg.

Calculate net protein utilization, digestibility and biological value.

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[5123]-415

M.Sc. - II

ANALYTICAL CHEMISTRY

CHA - 490 : Analytical Spectroscopy
(2013 Pattern) (Semester - IV)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic table/non-programmable calculator is allowed.

SECTION - I

Q1) Answer the following questions: [10]

a) State and explain the principle of ultraviolet photoelectron spectroscopy.
b) State the applications of electron spectroscopy of chemical analysis.
c) What are collimators? Explain the necessity of collimation in X-ray analysis.
d) Explain the absorptive edge method for qualitative analysis.
e) What are the limitations of the human eyes? How it overcome by microscope?

Q2) Attempt any two of the following: [10]

a) Explain the different components of SEM. How do we get images by SEM?
b) What are the satellite peaks? Explain the origin of ESCA satellite peaks.
c) With schematic diagram, explain the working of X-ray diffraction powder camera.
d) The Kα line of magnesium at 989.0 pm was used to perform quantitative analysis of cadmium in an aqueous solution with the analyte in the X-ray fluorescence instrument. The detector response of aqueous sample and 100 ppm cadmium standard solution was 3560 counts in 10 seconds and 2000 counts per second respectively. Calculate the concentration of cadmium in water sample.

P.T.O.
Q3) Attempt any one of the following:  

a) The 1S electron has binding energy 1080.5 eV and the work function of ESCA spectrometer is 7.98 eV, if the incident radiation of Cu, Kα (λ = 0.154 nm). Calculate the kinetic energy of measured electron. (Given: Planck’s constant = 6.625 × 10⁻³⁴ Js, velocity of light = 3 × 10⁸ m/s).

b) What are analysers? Explain the working of magnetic field analyser.

SECTION - II

Q4) Answer the following questions:  

a) What is Nuclear Overhauser Effect?

b) What is recombination fluorescence?

c) Explain heavy atom effect with suitable example in fluorescence.

d) Explain electron transitions during photoluminescence.

e) What is spin-spin splitting?

Q5) Attempt any two of the following:  

a) Describe components involved with block diagram in chemiluminescent apparatus.

b) Give different applications of ¹H NMR in quantitative analysis.

c) Discuss the factors affecting on photoluminescence.

d) Calculate the chemical shift of a particular nucleus in 60 MHz instrument if the reference nucleus absorbs at a magnetic flux density that is 0.063 G greater than that at which the sample nucleus absorbs. (Given: For proton Bo = 14092 G)

Q6) Attempt any one of the following:  

a) Explain analysis of non-luminescing compound with suitable examples.

b) Discuss the ¹H, ¹⁹F and ³¹P NMR spectra for (CH₃)₂ PC F₂CH₃ compound.
ANALYTICAL CHEMISTRY
CHA - 491 : Analytical Methods for Analysis of Fertilizers,
Detergents, Water, Polymer, Paint and Pigment
(2013 Pattern) (Semester - IV)

Time : 3 Hours] [Max. Marks : 50

Instructions to the candidates:
1) All questions of respective section are compulsory.
2) Figures to right hand side indicate full marks.
3) Neat labelled diagram must be drawn wherever necessary.
4) Use of log-table / non-programmable calculator is allowed.
5) Write the answers of two sections on separate answer books.

SECTION - I

Q1) Answer the following: [10]
   a) What is Saponification value?
   b) Enlist alcohol soluble material found in detergents.
   c) How free water is determined from fertilizer?
   d) Explain the terms:
      i) DO
      ii) BOD
   e) Give the principle for determination of lead by dithiozone method.

Q2) Attempt any two of the following: [10]
   a) Outline the procedure for determination of Nitrogen by Kjeldahls method.
   b) Discuss a method to extract and estimate unsulphonated and unsulphated material from sample of detergent.
   c) Explain analytical method for the determination of Arsenic from waste water.

P.T.O.
d) A 0.401g of sample of commercial phosphate detergent was ignited at red heat to destroy organic matter. The residue was taken up in hot HCl which converts the phosphorus to $\text{H}_3\text{PO}_4$. The phosphate was precipitated as $\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}$ by addition of $\text{Mg}^{2+}$ ions followed by aqueous $\text{NH}_3$. After filtration and washing, the precipitate was converted to $\text{Mg}_2\text{P}_2\text{O}_7$ by ignition to 1000°C. The weight of the residue was found to be 0.262g. Calculate the percentage of phosphorus in the sample.

**Q3)** Attempt any one of the following: [5]


b) Give a suitable method for estimation of equivalent combined $\text{SO}_3$ from detergent sample.

**SECTION - II**

(Polymer Analysis)

**Q4)** Answer the following: [10]

a) Explain ‘Impact test’ and ‘abrasion resistance’.

b) Define ‘emulsion paints and enamels’.

c) Define glass transition temperature.

d) Give classification of polymer.

e) How Mechanical properties can be used in Physical testing of polymer?

**Q5)** Answer any two of the following: [10]

a) Distinguish between addition and condensation polymerisation.

b) Explain identification of binders from paints.

c) Explain the method to determine molecular weight of polymer by viscosity measurement.

d) A 250 mg of yellow chrome pigment was disintegrated and the soluble chromate was extracted with sulphuric acid. The volume of the solution was made up to 100 ml. A 25.0ml aliquot of this solution was used for chromate estimation iodometrically, which required 12.7ml of standard 0.05N sodium thiosulphate for complete reaction. Calculate the percentage of $\text{CrO}_3$ in the given pigment sample.

(Given: Atomic wt. of Cr = 51.99)
Q6) Answer any one of the following:

a) What are pigments? Discuss the analytical method for the estimation of zinc from the pigment sample.

b) 0.8321 gm of carboxyl terminated polybutadiene was dissolved in mixture of ethanol and toluene. The mixture was titrated with 0.1234N alcoholic KOH using Phenolphthalein as an indicator. The burette reading was 7.8ml. Calculate the number average molecular weight of polymer.

(Given: Functionality = 2).
M.Sc. - II
ANALYTICAL CHEMISTRY
CHA-492: Methods of Analysis and Applications
(2013 Pattern) (Semester - IV)

Time: 3 Hours] [Max. Marks: 50

Instructions to the candidates:
1) Students should attempt any two sections from Section I, II and III.
2) All questions of respective sections are compulsory.
3) Figures to right hand side indicate full marks.
4) Neat labelled diagram must be drawn wherever necessary.
5) Use of log table / non-programmable calculator is allowed.
6) Write the answers of two sections on separate answer book.

SECTION - I
Pollution Monitoring and Control

Q1) Answer the following: [10]
   a) Give advantages of liquid scrubber.
   b) What is desulphurization of fuel?
   c) What are the sources of NOX?
   d) Describe ‘Industrial effluent’.
   e) State the principle of chemical coaguation method.

Q2) Attempt any two of the following: [10]
   a) Explain the separation of particulate matter using stream exchange technique.
   b) Describe in detail a method for determination of mercury from Water.
   c) Write a short note on control measures of NOX.
   d) Describe a suitable method for removal of fertilizers and nitrites from waste water.

P.T.O.
Q3) Attempt any one of the following:  

a) Discuss the hazardous effects of SO₂ on human health. How it is controlled?

b) Explain the principle and working of electrostatic precipitator.

SECTION - II
Analysis of Body Fluids

Q4) Attempt the following:  

a) What are body fluids?

b) Write the structure and functions of bilirubin.

c) Write the principle of radioimmunoassay.

d) Write sources and deficiency diseases of thiamine.

e) What are the causes of increased and decreased levels of serum phosphate?

Q5) Attempt any two of the following:  

a) What is
   i) Hypernatraemia
   ii) Hyponatraemia
   iii) HyperKalaemia
   iv) Hypokalaemia

b) How urine is collected and preserved for analysis? What changes takes place on keeping urine?

c) Discuss the chemistry of Vit. B₁₂ w.r.t. structure, sources, biological functions and principle of estimation.

d) Two patients have blood urea of 80 Mg% and 75 Mg%. If urinary urea of both patients is 2100 Mg% and rate of urine flow is 2 ml/min and 1 ml/min respectively. Calculate the urea clearance of each patient and comment on results.
Q6) Attempt any one of the following:

a) Discuss the practical application of radioimmunoassay in progesterone determination.

b) Unknown urine sample of four patients were analysed for glucose content by Benedict’s method. The volume of Benedict’s solution required by each sample is as below:

<table>
<thead>
<tr>
<th>Patient No. No. of times sample is diluted</th>
<th>Volume of Benedict’s solution (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>09</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

Calculate the grams of glucose per 100 ml of the sample of each patient.

SECTION - III

Carbon Nanostructures and Applications of Nanotechnology

Q7) Attempt the following:

a) Explain the structure of alkali doped C_{60} Molecule.

b) Define photodynamic therapy in targeted drug administration.

c) Enlist the different types of biosensors.

d) Give different types of bacteria used in synthesis of nanoparticles.

e) Explain in short field emission CNT’s.
Q8) Answer any two of the following: [10]
   a) Explain any two properties of nanotubes.
   b) Explain the terms:
      i) Intercalation.
      ii) Electrochemical sensors.
   c) How nanomaterials cause potential health hazards?
   d) Explain in brief DNA based nanomaterials as biosensors.

Q9) Answer any one of the following: [5]
   a) Describe toxic effects of nanomaterials.
   b) Explain the fabrication of carbon nanotubes.
PHYSICAL CHEMISTRY

CHP - 110: Fundamentals of Physical Chemistry - I
(2014 Pattern) (Semester - I)

Time : 3 Hours]

Instructions to the candidates:

1) Answer to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right side indicate full marks.
4) Use of logarithmic table /calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1. Avogadro Number
   \( N = 6.022 \times 10^{23} \text{ mol}^{-1} \)

2. Boltzmann Constant
   \( k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} \)
   \( = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \)

3. Planck Constant
   \( h = 6.626 \times 10^{-27} \text{ erg s} \)
   \( = 6.626 \times 10^{-34} \text{ J s} \)

4. Electronic Charge
   \( e = 4.803 \times 10^{-10} \text{ esu} \)
   \( = 1.602 \times 10^{-19} \text{ C} \)
   \( = 23.06 \text{ k cal mol}^{-1} \)
   \( = 1.602 \times 10^{-12} \text{ erg} \)
   \( = 1.602 \times 10^{-19} \text{ J} \)
   \( = 8065.5 \text{ cm}^{-1} \)

5. 1 eV

6. Gas Constant
   \( R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} \)
   \( = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
   \( = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \)

7. Faraday Constant
   \( F = 96487 \text{ C equiv}^{-1} \)

8. Speed of light
   \( c = 2.997 \times 10^{10} \text{ cm s}^{-1} \)
   \( = 2.997 \times 10^{8} \text{ m s}^{-1} \)
   \( = 4.184 \times 10^{7} \text{ erg} \)
   \( = 4.184 \text{ J} \)

9. 1 cal

10. 1 amu
    \( = 1.673 \times 10^{-27} \text{ kg} \)

11. Bohr magneton
    \( \beta_e = -9.274 \times 10^{-24} \text{ J T}^{-1} \)

12. Nuclear magneton
    \( \beta_n = 5.051 \times 10^{-27} \text{ J T}^{-1} \)

13. Mass of an electron
    \( m_e = 9.11 \times 10^{-31} \text{ kg} \)

P.T.O.
SECTION -I

Q1) Attempt the following: [10]

a) Write Gibbs - Helmholtz equation and give the significance of the terms involved in it.

b) What is photoelectric effect? Give its practical application.

c) Define the terms work, heat and energy.

d) State Raoult’s and Henry Law.

e) Give inadequacies of first law of thermodynamics.

Q2) Attempt any two of the following: [10]

a) Show that, depression in freezing point is a colligative property.

b) Sketch and explain the phase diagram for Helium.

c) Define chemical potential. Derive the expression for the change in entropy when two ideal gases are mixed.

d) State the third law of thermodynamics. Give the relation between equilibrium and spontaneity of reaction.

Q3) Solve any one of the following: [5]

a) An electron of mass ‘m’ confined to a one dimensional box of length ‘b’. If it makes a radiative transition from second excited to the ground state. Calculate the frequency of the photon emitted.

b) The partial molar volumes of acetone and chloroform in their mixture in which the mole fraction of chloroform is 0.4693, are 74.17 and 80.24 cm³/mole respectively. What is the volume of a kg solution of the above mixture?

[At.wts., C=12, Cl=35.5, O =16, H = 1]
SECTION - II

Q4) Attempt the following: [10]

a) Discuss steady state principle with example.

b) Give the Eyring equation and explain the terms their in.

c) Explain Bose - Einstein statistics.

d) For the reaction \(2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}\), the experimental rate law is \(r = K[\text{NO}_2][\text{F}_2]\). Propose the mechanism of reaction.

e) Define the terms ‘Energy of Activation’ and ‘frequency factor’.

Q5) Attempt any two of the following: [10]

a) Describe the relaxation technique used to study fast reactions and give the expression for relaxation time for a first order reaction.

b) What are diffusion controlled limits? Derive the equation for diffusion controlled reaction.

c) Obtain an expression for Boltzmann distribution law.

d) Discuss the Lindemann’s theory for unimolecular reaction.

Q6) Solve any one of the following: [5]

a) The rate constant for a reaction at 300K is \(1.352 \times 10^{-2} \text{ s}^{-1}\) and its frequency factor is \(2.785 \times 10^6 \text{ s}^{-1}\). Determine enthalpy and entropy of activation.

b) Calculate the diffusion controlled rate coefficient 25°C for the species in n-pentane. Given the viscosity of n-pentane is 0.22 g. m\(^{-1}\).s\(^{-1}\).
P1416

[5123]-1002

M.Sc.- I

INORGANIC CHEMISTRY

CHI-130: Molecular Symmetry and Chemistry of p-block Elements
(2014 Pattern) (New -4 Credit System) (Semester - I)

Time : 3 Hours

Instructions to the candidates:

1) All questions are compulsory.
2) Answers to the two sections should be written in separate answer books.
3) Figures to the right indicate full marks.
4) Use of log tables/character tables and calculator is allowed.

SECTION - I

Q1) Answer the following: [10]

a) List out the subgroups of D₂ point group.

b) Find out the product of C'₂ × σₓ by matrix multiplication method.

c) Mention the symmetry elements, order and classes of D₃h point group.

d) Write down all the associative operations with S₄ axis.

e) How do you distinguish between C₃v and C₃h point group using suitable examples?

Q2) Attempt any two of the following: [10]

a) Define plane of symmetry. Explain different types of planes of symmetry using Fe(CO)₅ molecule.

b) Classify cis - platin in the appropriate point group. Justify your answer.

c) Derive the character table for C₂ᵥ point group using great orthogonality theorem.

d) On the basis of symmetry what is the correct criterion for the molecule to be optically active? Which of the following molecule is optically active?
   i) CHFBrCl                    ii) CHClF₂

P.T.O.
**Q3** Attempt **any one** of the following: 

a) For \([\text{FeCl}_4]^2-\) considering sigma bond as basis of representation find the reducible representation and find out the orbitals that are offered for sigma bonding.

b) Find out the normalized SALC using projection operator \(E_u\) irreducible representation which operates on \(\sigma_i\) orbital of \([\text{Ni(CN)}_4]^2-\) ion.

\[
\begin{array}{ccccccccc}
D_{4h} & E & 2C_4 & C_2 & 2C'_2 & 2C''_3 & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\
E_u & 2 & 0 & -2 & 0 & 0 & -2 & 0 & 2 & 0 & 0 \\
\end{array}
\]

**SECTION-II**

**Q4** Answer the following:

a) Give classification of hydrides with example.

b) Mention the different processes used for activation of nitrogen.

c) Give preparation reaction of RMgX. What precaution is to be taken during preparation of RMgX.

d) How alkali metals in ammonia acts as a reducing agent? Explain.

e) What are interhalogen compounds? Mention types.

**Q5** Attempt **any two** of the following:

a) Write a note on aluminosilicates.

b) Give an account of borazole.

c) Give an account of oxyacids of halogens.

d) Write a note on fullerenes.
Q6) Draw any five structures.

a) $\text{B}_4\text{H}_{10}$

b) $\text{ClF}_3$

c) $\text{IF}_7$

d) $\text{Si}_3\text{O}_{9}^-$

e) $\text{P}_4\text{O}_{10}$

f) $[\text{Cl}_2\text{PN}]_3$

g) $\text{B}_3\text{N}_3\text{H}_6$

Given:

Character table for $T_d$ point group.

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>E</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$T_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$T_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

- $x^2+y^2+z^2$
- $(2z^2-x^2-y^2, x^2-y^2)$
- $(R_x, R_y, R_z)$
- $(x, y, z)$
- $(xy, xz, yz)$
SECTION -I

Q1) Attempt the following: [5]

a) Explain with suitable example benzeroid and nonbenzeroid compounds.

b) Comments on the conformational analysis of acyclic compounds.

c) Annulenes are aromatic. Why?

d) Discuss in brief stereoselective reactions.

e) Explain diastereomeric relationship.

Q2) Attempt any five of the following: [10]

a) Comment on the aromaticity of the following:

\[ \text{and} \]

P.T.O.
b) Explain structure and stability of carbenes.
c) Write short note on prochiral relationship.
d) Write short note on benzeroid compounds.
e) Comment on the optical activity of the following with justification.

\[
\begin{align*}
H_2N & \quad \text{and} \quad NH_2 \\
& \quad \text{H}
\end{align*}
\]

f) Assign Re and Si face labels to the following Acetophenone.

\[
\begin{align*}
& \quad H \\
& \quad m_e \\
& \quad O
\end{align*}
\]

\[
\begin{align*}
& \quad H \\
& \quad m_e \\
& \quad O
\end{align*}
\]

Q3) Attempt any five of the following: [10]

a) Explain which of the following will have higher pka value.

\[
\begin{align*}
\text{CH}_3 & \quad \text{and} \quad \text{Cl} \\
& \quad O
\end{align*}
\]

b) Write short note on Inductive effect affecting basicity.

c) Assign E/Z designation to the followings.

\[
\begin{align*}
& \quad \text{HS} \\
& \quad \text{CH}_2\text{OH} & \quad \text{and} \quad \text{Cl} \\
& \quad \text{CH}_2\text{Cl}
\end{align*}
\]

d) Assign R/S label to the chiral carbons and justify.

\[
\begin{align*}
& \quad \text{Ph} \\
& \quad \text{H} \\
& \quad \text{H} \\
& \quad \text{H}_2\text{C} - \text{C}^* - \text{C}^* \quad \text{Ph} \\
& \quad \text{Br} \\
& \quad \text{H}
\end{align*}
\]
e) What is the stereochemical relationship between the following compounds?

\[ \text{CH}_2\text{Br} \quad \text{NO}_2 \quad \text{and} \quad \text{CH}_2\text{Br} \quad \text{NO}_2 \]

f) Write equivalent structures

\[ \text{CHO} \quad \text{Cl} \quad \text{me} \quad \text{CH}_2\text{CH} \quad \equiv \quad ? \quad ? \quad \text{CHO} \quad ? \quad ? \quad \equiv \quad ? \quad ? \quad \text{CH}_2\text{OH} \]

**SECTION -II**

**Q4)** Answer the following: [5]

a) Explain chemoselectivity in addition reactions.

b) What is SNi mechanism?

c) Discuss in brief conjugate addition.

d) Explain non-classical carbocation with suitable example.

e) What is different between E2 and E1cb mechanism.

**Q5)** Suggest the mechanism (any five): [10]

a) \[ 2\text{PhCH} = \text{CH}_2 \xrightarrow{\text{H}^+} \text{ph} \]

b) \[ \text{F} \quad \text{Me}_3 \text{O} \quad \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{F} \quad \text{Me}_3 \text{O} \quad \text{NO}_2 \]
Q6) Predict the products (Any five):

[10]

a) \[ \text{Anisole} \xrightarrow{\text{H}_2\text{O}_2} \] \[ ? \xrightarrow{\text{Br}_2} \] \[ ? \xrightarrow{\text{FeBr}_3} \] 

b) \[ \text{ } \text{ } \text{ } + \text{CHCl}_3 \xrightarrow{i)} \text{alc. KOH} \] \[ \xrightarrow{ii) \text{H}_2\text{O}} ? \] 

[5123] - 1003
c) \[ \text{cyclohexane} \xrightarrow{\text{NB3, H2O}} ? \]

d) \[ \text{ThS=O - C6H5-CH=CH-C6H5} \xrightarrow{\Delta} ? \]

e) \[ \text{n-PrO} \xrightarrow{\text{?}} \]

f) \[ \text{cyclopentene} \xrightarrow{\text{EtO K+}} \text{?} \]

g) \[ \text{?} \xrightarrow{\text{BH3, THF}} \xrightarrow{\text{H2O2/O2}} ? \]

EEE
M.Sc.-I

ANALYTICAL CHEMISTRY

CHA-190: Safety In Chemical Laboratory and Good Laboratory Practices

(2014 Pattern) (Credit System) (4-Credits) (New) (Semester-I)

Time : 3 Hours

Instructions to the candidates:

1) Answer to the two sections should be written in separate answer books.
2) All the questions are compulsory.
3) Neat diagram must be drawn wherever necessary.

SECTION-I

Q1) Answer the following: [10]

a) Discuss the importance of safety and security in chemical laboratory.
b) What are the types of gloves used in laboratory?
c) What are the materials required in first aid box.
d) What do you mean by good house keeping.
e) Explain the term:
   i) Irritants.
   ii) Toxic substance.

Q2) Answer any two of the following: [10]

a) Which precautions should be taken during handling of accidental released substances.
b) Discuss the various steps involved in security chemicals of concern.
c) Explain the role of safety goggles and face shield in laboratory.
d) How will you classify the waste materials.

P.T.O.
Q3) Attempt any one of the following: 
   a) Discuss the different types of disposal methods in hazardous chemicals.
   b) Write short note on personnel protective equipments.

SECTION-II

Q4) Answer the following: 
   a) What is mean by G-Lp?
   b) Explain the importance of study plan protocol.
   c) What are the precautions taken during handling of Flammable substances.
   d) Explain acid spillage in short.
   e) Explain the dry CO₂ fire extinguisher.

Q5) Answer any two of the following: 
   a) What is the principle of SOP? How it is implemented in laboratory.
   b) Explain the term waste classification.
   c) What are the general guidelines for chemical storage?
   d) What are the types of accidents occurs in laboratory? Mention the precautions to avoid it.

Q6) Attempt any one of the following: 
   a) Explain any two methods of calibration of equipments.
   b) Sketch and label the structure of safety chemistry laboratory as per safety rules and explain it in brief.

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P1419

[5123] - 2001

M.Sc.

PHYSICAL CHEMISTRY

CHP - 210: Fundamentals of Physical Chemistry -II
(2014 Pattern) (Semester - II) (4 Credit) (New)

Time : 3 Hours] [Max. Marks :50

Instructions to the candidates:

1) Answer to the two sections should be written in separate answer books.

2) All questions are compulsory.

3) Figures to the right side indicate full marks.

4) Use of logarithmic table calculator is allowed.

5) Neat diagrams must be drawn wherever necessary.

Physico - Chemical Constants

1. Avogadro Number
   \[ N = 6.022 \times 10^{23} \text{ mol}^{-1} \]

2. Boltzmann Constant
   \[ k = 1.38 \times 10^{-16} \text{ erg K}^{-1} \text{ molecule}^{-1} \]
   \[ = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1} \]

3. Planck Constant
   \[ h = 6.626 \times 10^{-27} \text{ erg s} \]
   \[ = 6.626 \times 10^{-34} \text{ J s} \]

4. Electronic Charge
   \[ e = 4.803 \times 10^{-10} \text{ esu} \]
   \[ = 1.602 \times 10^{-19} \text{ C} \]

5. 1 eV
   \[ = 23.06 \text{ k cal mol}^{-1} \]
   \[ = 1.602 \times 10^{-12} \text{ erg} \]
   \[ = 1.602 \times 10^{-19} \text{ J} \]
   \[ = 8065.5 \text{ cm}^{-1} \]

6. Gas Constant
   \[ R = 8.314 \times 10^{7} \text{ erg K}^{-1} \text{ mol}^{-1} \]
   \[ = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]
   \[ = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \]

7. Faraday Constant
   \[ F = 96487 \text{ C equiv}^{-1} \]

8. Speed of light
   \[ c = 2.997 \times 10^{10} \text{ cm s}^{-1} \]
   \[ = 2.997 \times 10^{8} \text{ m s}^{-1} \]
   \[ = 4.184 \times 10^{7} \text{ erg} \]
   \[ = 4.184 \text{ J} \]

9. 1 cal
   \[ = 1.673 \times 10^{-27} \text{ kg} \]

10. 1 amu
    \[ \beta_e = -9.274 \times 10^{-24} \text{ J T}^{-1} \]

11. Bohr magneton
    \[ \beta_s = 5.051 \times 10^{-27} \text{ J T}^{-1} \]

12. Nuclear magneton
    \[ m_e = 9.11 \times 10^{-31} \text{ kg} \]

P.T.O.
SECTION -I

Q1) Attempt the following: [10]

a) What is signal to noise ratio?

b) What is the effect of isotopic substitution on the nature of the rotational spectrum?

c) What is Franck-condon principle?

d) What is a breathing frequency? Explain with an example.

e) Distinguish between harmonic and anharmonic oscillator with respect to

i) Energy expression

ii) Selection rule

Q2) Attempt any two of the following: [10]

a) Sketch the polarizability ellipsoid for fundamental vibrational modes of CO₂ molecule and explain its Raman activity.

b) Explain the Fortrat diagram for B' < B''.

c) What is centrifugal distortion constant? Derive the relation between centrifugal distortion constant (D) and rotational constant (B).

d) How is the value of B calculated from the vibrational rotational spectrum under poor resolution?

Q3) Attempt any one of the following: [5]

a) The rotational constant for H³⁵Cl is observed to be 10.5909 cm⁻¹. What is the value of B for H³⁷Cl?

b) IR spectra of ¹⁴N¹⁶O shows an intense spectral line at 1876.06 cm⁻¹ followed by less intense spectral line at 3724.20 cm⁻¹. Evaluate the equilibrium vibrational frequency and an anharmonicity constant for the molecule.
SECTION -II

Q4) Answer the following: [10]
   a) Describe a method to determine the concentration of radio-iodine in the spent fuel.
   b) Define Rad and Rontgen. Give their interrelation.
   c) What is the effect of applied voltage on current pulse height?
   d) What is Fick’s first law? Give its limitation.
   e) How does 3H synthesized artificially and naturally?

Q5) Attempt any two of the following: [10]
   a) Write a note on organic and inorganic scintillators.
   b) Explain the working of a breeder reactor using uranium-thorium as a fissile-fertile isotope pair.
   c) What are the effects of r-ray deposition in matter? Explain the photoelectric effect in detail.

Q6) Solve any one of the following: [5]
   a) An ancient coin (mass = 0.1 g) containing Cu was irradiated for 2 min. in a nuclear reactor with thermal neutron flux component \(1.5 \times 10^{11}\) n.cm\(^{-2}\).s\(^{-1}\) where \(^{63}\)Cu(n, r)^{64} Cu reaction takes place. The activity was determined after the cooling period of 6 h and was found to be 10000 dps. Calculate the amount of Cu in the coin sample. [Given: \(t_{1/2}\) of \(^{64}\)Cu = 12.7 h, \(\sigma=4.5\) b, r-ray abundance = 69.17%]
   b) Find the thickness of Al sheet required to reduce the activity from a r. source from 3500 dps to 650 dps. [Given: \(\mu_c = 0.211\) b/e, \& of Al = 2.1 g/cm\(^3\)"

EEE

[5123] - 2001  3
INORGANIC CHEMISTRY

CHI - 230 : Co-Ordination and Bioinorganic Chemistry

(2014 Pattern) (New 4 - Credits) (Semester - II)

Time : 3 Hours

Instructions to the candidates:
1) All questions are compulsory.
2) Answers to the two sections should be written in separate answer books.
3) Neat and labelled diagrams must be drawn wherever necessary.
4) Figures to the right indicate full marks.
5) Given : Atomic number \[ \text{C}_6 = 27; \text{I}_r = 77; \text{F}_r = 26 \]

SECTION - I

**Q1** Answer the following questions: [10]

a) Find the possible term symbol(s) of the excited state of K atom with the electronic configuration \([1S^2 2S^2 2P^6 3S^2 3P^6 4P^1]\).

b) Identify which of the following complex ions shows same spin values.
   i) \([C_6F_6]^{3-}\)
   ii) \([I_rCl_6]^{3-}\)
   iii) \([F_rF_6]^{3-}\)

c) Determine the total degeneracy and orbital states for tzg\(^1\) eg\(^1\) configuration in strong octahedral field using direct product table.

d) Give energy level diagram of \(C_r\) (III) ion in octahedral field.

e) Give Hund’s rule for determination of ground state term symbol. Illustrate with suitable example.

**Q2** Attempt any two of the following: [10]

a) Prepare a table of microstates and hence obtain the allowed R.S. terms for the (h - 1) \(S^1 np^1\) configuration.

**P.T.O.**
b) Arrange the following transitions in octahedral complex according to increasing intensity

i) \( A_{2g} \rightarrow A_{1g} \)

ii) \( 2_{Eg} \rightarrow 2_{Eg} \)

iii) \( A_{2u} \rightarrow T_{2g} \)

c) Find out how degeneracy of ground R-S term of Co\(^{2+}\) ion looses on complex formation as \([\text{Co(H}_2\text{O)}_6]^{2+}\).

d) For a complex three absorption bands ave observed at 17500 cm\(^{-1}\) (charge transfer), 24700 cm\(^{-1}\) and 37 900 cm\(^{-1}\). Determine \( \Delta_0 \) and racah parameter. Comment on nature of M - L bond. [\( B_0 \) for M\(^{\text{III}} \) 914 cm\(^{-1}\)].

**Q3** Attempt any one of the following: [5]

a) Write a note on quenching of orbital magnetic moment by crystal field.

b) Discuss the selection rules in d - d transitions including relaxation.

**SECTION - II**

**Q4** Answer in short: [10]

a) Explain the role of potassium in biological system.

b) Mention the metal proteins involved in electron transfer reactions.

c) Cis platin is used as anticancer drug and not transplation. Explain.

d) Differentiate between ferritin and transferrin.

(e) Explain oxygen transport in mammals.

**Q5** Attempt any two of the following: [10]

a) Give classification of biomolecules.

b) Explain detoxification of mercury.

c) Give an account of zinc finger.

d) Explain in detail structure of RNA.
Q6) Attempt any one of the following:

a) Draw the structures:
   i) Corrin
   ii) Vit. B₁₂
   iii) Auranofin
   iv) Aspartate
   v) Thyamine

OR

b) Match the following:
   i) Na    a) N₂ fixation
   ii) Fe   b) Calmodulin
   iii) Hg  c) O₂ transport
   iv) Ca   d) Osmotic balance
   v) V     e) Detoxification
### Charge Table for Diamagnetic Group

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### Correlation Table for the Group \(O\)_\(_h\)

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DIRECT PRODUCTS

1. Groups of the form $G \times G$ for $G \times G$:
   The $e$, $u$ or $i$ additions to the VR symbols in their group satisfy:
   $e \times e = u \times u = e$, $u \times u = i$, $i \times i = u$.

2. Products of the form $A \times A$, $B \times B$, $A \times B$:
   For all groups:
   - Letter symbols: $A \times A = A$, $B \times B = B$, $A \times B = B$.
   - Subscripts: $1 \times 1 = 1$, $2 \times 2 = 1$.
   - Except for the $B$ representations of $D_2$ and $D_4$ where:
     $B \times B = B$ and $1 \times 2 = 2$, $2 \times 3 = 1$, $3 \times 1 = 2$.

3. Product of the form $A \times B$:
   (a) For all groups: $A \times B = B$, irrespective of the suffix on $A$.
   (b) For all groups except $D_4$, $D_6$, $S_3$:
       $A \times B = B$, $B \times B = A$.
       (irrespective of the suffix on $B$. (If the group has only one $B$ representative,
       put $B \times B = A$.)
   (c) For $D_4$:
       $B \times B = B$, $B \times B = B$.
       (irrespective of the suffix on $B$.
   (d) For $D_6$, $S_3$:
       $B \times B = B$, $B \times B = B$.
       (irrespective of the suffix on $B$.

4. Products of the form $B \times B$:
   (For groups which have $A$, $B$ or $C$ symbols without suffix, put $A_1 = A_2 = A_3$,
   etc. in the equations below.)
   (a) For $C_4$, $D_4$, $D_{4v}$, $C_{4v}$, $C_{4v}$, $C_{4v}$, $D_2$, $C_{2v}$, $C_{2v}$, $C_{2v}$, $C_{2v}$, $C_{2v}$:
       $B_1 \times B_1 = B_1 \times B_1 = B_1$, $B_1 \times B_1 = B_1$, $B_1 \times B_1 = B_1$,
       $B_1 \times B_1 = B_1$, $B_1 \times B_1 = B_1$.
   (b) For $D_{4v}$, $D_{2v}$, $C_{2v}$, $C_{2v}$, $B_1$, $B_2$:
       $B_1 \times B_1 = B_1$, $B_1 \times B_1 = B_1$, $B_1 \times B_1 = B_1$.
   (c) For $D_4$:
       $E_1 \times E_1 = E_1 \times E_1 = E_1 \times E_1 = E_1 \times E_1 = E_1 \times E_1 = E_1$, $E_1 \times E_1 = E_1$, $E_1 \times E_1 = E_1$, $E_1 \times E_1 = E_1$. [5123]-2002 5
### Table: Mathematical Expressions

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#### 5. Products involving the T (or T') representations of O and T:

- For D

\[
E \times E = A_1 + A_3 + B_1 + B_3
\]

- For D'

\[
E \times E = A_1 + A_4 + B_2 + B_5
\]
P1421

[5123]-2003
M.Sc. - I
ORGANIC CHEMISTRY
CHO - 250 : Synthetic Organic Chemistry and Spectroscopy
(2014 Pattern) (Semester - II)

Time : 3 Hours

Instructions to the candidates:
1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory.
3) Figures to the right indicate full marks.

SECTION - I

Q1) Explain any five of the following: [10]

a) Cyclohexene on treatment with O₃O₄ gives cis diol while with per acid followed by hydrolysis gives transdiol.

b) 2-Hydroxy acetophenone can not be prepared by direct acylation of phenol but can be easily prepared by Fries rearrangement of phenyl acetate.

c) Organolithium reagents shows 1, 2 - addition to α, β unsaturated compound, while organocuprates shows 1, 4 - addition.

\[ \begin{align*}
  &\text{Ph} \\
  &\text{Ph} \\
  &\text{F₃C-C-} \quad \text{F₃C-C} \\
  &\text{OH} \quad \text{OH}
\end{align*} \]

d) The compound is resistant to pinacol-pinacolone rearrangement.

e) Beckmann rearrangement is an antimigration type reaction. Explain with suitable example.

f) Anisole on reaction with Na, liquid NH₃ in alcohol gives 2, 5 - dihydroderivatives.

Q2) Attempt any five of the following: [10]

a) Simmons - Smith reaction.

b) Grignard Reaction.

P.T.O.
c) Withing-Horner - Emmons reaction
d) Claisen rearrangement.
e) Moffatt oxidation.
f) Sulfur ylides.

**Q3** Predict the products and suggest the mechanism Any Two:  

\[ \text{cyclohexene} \xrightarrow{m-CPBA} \quad \text{product} \]
\[ \text{MeO} \xrightarrow{\text{DIBAL-H, } \text{MeOH}} \quad \text{product} \]
\[ \text{compound} \xrightarrow{\text{H}_2, \text{Willeminson's catalyst}} \quad \text{product} \]
\[ \text{Ph_3P=CHOME} \xrightarrow{2- \text{H_3O+}} \quad \text{product} \]

**SECTION - II**

**Q4** Answer any five of the following:

a) Calculate the \( \lambda_{\text{max}} \) for the following compounds:

i) 

ii) 

b) Write a note on spin-spin splitting.

c) In IR spectroscopy, 2- chlorocyclohexanenace absorbs at two frequencies at 1725 cm\(^{-1}\) and 1745 cm\(^{-1}\). Explain.
d) How will you monitor the following reaction sequence by IR. Suggest the reagents

\[ \text{[Diagram]} \]

\[ \text{[Diagram]} \]

\[ \text{[Diagram]} \]


e) Give the genesis of the following compounds in mass spectrometry.

i) \( \text{[Chemical Structure]} \)
136, 135, 119, 107, 92, 77, M+

ii) \( \text{[Chemical Structure]} \)
M+97, 82, 68, 57, 54, 41, 40

f) How will you distinguish the following compounds by PMR

\[ \text{[Diagram]} \] and \[ \text{[Diagram]} \]

Q5) Deduce the structure of any five of the following compounds using spectral data and justify your answer.

[10]

a) M.F. \( \text{C}_{10}\text{H}_{11}\text{NO}_4 \)
IR : 1735, 1530, 1350, cm\(^{-1}\).
PMR : \( \delta \) 1.3 (t, 7H\(_2\), 12mm), 2.6 (S, 12mm), 4.25 (q, 7H\(_2\), 8mm), 7.4(d, 8H\(_2\), 4 mm), 7.9 (dd, 8 & 2Hz, 4mm), 8.3 (d, 2H\(_2\), 4mm).

b) MF - \( \text{C}_{5}\text{H}_{100} \)
IR: 2850, 2720, 1710 cm\(^{-1}\).
PMR : \( \delta \) 1.01 (d, 7H\(_2\), 6H), 2.06 (m, 1H), 2.36 (t, 2H), 9.72 (t, 1H).

c) M.F. : \( \text{C}_{6}\text{H}_{10}\text{O}\(_3\) \)
IR : 1745, 1710 cm\(^{-1}\).
PMR : \( \delta \) 1.21 (t, J = 7H2, 3H), 2-23 (S, 3H), 3.24 (2, 2H), 4.30 (q, 15, 7H\(_2\), 2H).

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d) MF: C₉H₉N
   IR : 2240, 1600, 1500 cm⁻¹.
   PMR : 8.2.3 (t, J = 7H₂, 6mm), 2.5 (t, J = 7H₂, 6mm) 7.2 (m, 15mm).

e) Two isomeric alcohols A & B with following data.
   Isomer A : 11.0 (q), 23(q), 33(t), 68(d) ppm.
   Isomer B : 18(q), 32(d), 67(t) pppm.

f) M.F. : C₅H₁₁Br
   IR : Nothing significant.
   PMR : 1.02 (d, J = 6H₂, 24mm), 1.65 (m, 4mm), 1.85
   (m, 8mm), 3.4 (t, 5 = 6H₂, 8mm).

**Q6)** Attempt any two of the following:  

a) Select the structure which is most consistent with the given spectroscopic data.

   CMR: 27.5 (q), 29.5(t), 32.3 (s), 41.3(t), 46.6 (d), 211.5 (s).

   ![Structure i](image1.png)

   ![Structure ii](image2.png)

   ![Structure iii](image3.png)
b) Assign the chemical shifts with reasoning to the various protons in following compound.

3.97, S, 3H; 4.40, S, 3H;
5. sd, J = 2.5 H₂, 1H;
6.97d, J = 2.5H₂, 1H;
7.17, dd, J = 9 & 2H₂, 1H
7.40d, J = 2H₂; 1H;
8.07d, J = 9H₂, 1H.

c) Normally integration is not recorded in CMR explain.
PART - A

Modern Separation Methods and Hyphenated Techniques

Q1) Answer the following: [10]

a) Enlist different types of stationary phases used in Gas chromatography.

b) Explain the process of photoionization and thermal ionization in mass spectrometry.

c) Give the principle of ion-pair chromatography.

d) How is the resolving power of HPLC column increased?

e) What are the characteristics of an ideal detector?
Q2) Attempt any two of the following:  

a) Write a short note on Tandem mass spectrometry.

b) Compare the techniques of normal phase HPLC and reverse phase HPLC.

c) Give the classification of different chromatographic techniques based on stationary phase and mobile phase.

d) With the help of EI ionization method show the fragmentation of gaseous method and represent the mass spectrum of the ion fragments thus generated.

Q3) Answer any one of the following:  

a) Give names of the different detectors used in Gas chromatography and explain the working of flame ionization detector.

b) The following data was obtained by a gas-liquid chromatography on a 40cm packed column.

<table>
<thead>
<tr>
<th>Compound</th>
<th>t&lt;sub&gt;R&lt;/sub&gt; (min)</th>
<th>W(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) A</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>ii) B</td>
<td>10.4</td>
<td>0.75</td>
</tr>
<tr>
<td>iii) C</td>
<td>11.2</td>
<td>0.89</td>
</tr>
<tr>
<td>iv) D</td>
<td>15.3</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Calculate:

1) Average number of plates from the data.
2) The column resolution.
3) The plate height.
Total No. of Questions : 6

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M.Sc. - I
CHEMISTRY
CH - 290B: Basic Biochemistry
(2014-15 Pattern) (Semester - II) (4 Credits)

PART - B

Instructions to the candidates:
1) All questions are compulsory.
2) Answer to two sections to be written in separate answer books.
3) Figures to right indicate maximum marks.

SECTION - I

Q1) Answer any three of the following: [12]
   a) Describe various levels of structural organization in proteins.
   b) Discuss various models proposed to explain the function of cellular membrane. Which model has been accepted by the scientist. Why?
   c) Discuss the different reactions used for N terminal determination of peptide chain.
   d) What are lipids? Give different classes of lipids.

Q2) Explain any four of the following: [8]
   a) With suitable example, explain the properties of cell membrane that act as a barrier to the drug molecule.
   b) Active transport of solutes across membrane.
   c) α-helix.
   d) How protein engineering increases protein stability?
   e) Ninhydrin reaction.
   f) Titration curve of amino acid.

Q3) Attempt any two of the following: [5]
   a) Differentiate between starch and glycogen. Give their origin and biological function.
   b) Give classification of carbohydrates with suitable examples.
   c) Describe the pH scale and its importance in biological system.
SECTION - II

Q4) Answer any three of the following: [12]
   a) What do you understand by Immobilization of enzymes. Discuss different methods of Immobilization.
   b) Write an account on DNA replication.
   c) Write a note on fat soluble vitamins. Discuss biochemical functions & deficiency disorder.
   d) Discuss various types of inhibition of enzyme activity.

Q5) Explain the following (any four): [8]
   a) Translocation.
   b) Initiation, elongation and termination factors of protein synthesis.
   c) How enzymes can be utilized to manufacture certain pharmaceutical compounds.
   d) Role of macro and micro nutrients in the body.
   e) Role of water soluble vitamins in the body.
   f) Balanced diet and its importance.

Q6) Attempt any two of the following: [5]
   a) Give a short account of the following:
      i) Active site of enzyme
      ii) $K_m$ & its significance.
   b) Define the following terms:
      i) Cofactor
      ii) $V_{max}$
      iii) Allostery
      iv) Codons
      v) Introns
   c) What are intercalating agents? Explain how they interact with DNA molecule.
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[5123]-2004
M.Sc. - I
ANALYTICAL CHEMISTRY
CHA - 290: General Chemistry - II
(2014 Pattern) (Semester - II)
PART - C

Concept of Analytical Chemistry

Q1) Answer the following: [10]
   
   a) Distinguish between accuracy and precision.
   b) Explain in brief ‘T’ test.
   c) Calculate the proper number of significant figures in each of the following:
      i) 0.00256
      ii) 22.0092
   d) Give classification of nano-materials.
   e) Explain:
      i) Rounding off
      ii) Sampling of Liquids

Q2) Attempt any two of the following: [10]
   
   a) Write a short note on rejection of result in the ‘Q’ - test.
   b) What is an error? Explain the different types of errors.
   c) Give a brief account of:-
      i) Separation by precipitation.
      ii) Separation by distillation.
   d) What are the advantages of fused silica capillary columns compared with glass or metal columns.
Q3) Attempt any one of the following:

a) Give a brief account of :

i) Preparation of Laboratory sample.

ii) Automated Sample Handling.

b) A new automated procedure for determining glucose in serum (method A) is to be compared with the established method (method B). Both methods are performed on serum from the same six patients to eliminate patient to patient variability. Do the following results confirm a difference in the two methods at 95% confidence level?

[Given: ‘t’ value at 95% confidence level and 5 degrees of freedom = 2.57].

\[
\begin{array}{ccccccc}
\downarrow \text{method/patient} & 1 & 2 & 3 & 4 & 5 & 6 \\
\text{Method A} & 1025 & 780 & 840 & 810 & 950 & 655 \\
\text{Method B} & 1029 & 769 & 820 & 798 & 946 & 648 \\
\end{array}
\]
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[5123]-2004
M.Sc. - I
ANALYTICAL CHEMISTRY
CHA - 290: General Chemistry - II
(2014 Pattern) (Semester - II)
PART - D

Industrial Methods of Analysis

Q1) Answer the following: [10]

a) Calculate the number of millimoles present in 0.3g CaCO₃ (Ca = 40,
C = 12  O = 16)

b) What is common ion effect?

c) Define limiting reagent.

d) What is mmole and ppb?

e) Enlist different types of process analysers.

Q2) Attempt any two of the following: [10]

a) Explain the different quality systems in chemical laboratories.

b) Write a note on automatic elemental analyser.

c) What is a buffer? Explain the buffer action of acidic and basic buffer.

d) Explain stability and instability constants with suitable examples.
Q3) Answer any one of the following:

a) NiCl₂ is converted into [Ni(NH₃)₆] · Cl₂. Calculate the percentage of Nickel and nitrogen in the complex.

(Given at. wts: Ni = 58.6, N = 14, Cl = 35.5, H = 1)

b) Write a short note on: Responsibility of laboratory staff for quality.
P1422

M.Sc. - I

ORGANOMETALLIC AND INORGANIC REACTION MECHANISM

Q1) Answer the following: [10]

a) Give the rate law for the following reaction.

\[ ML_5X + X \rightleftharpoons ML_5Y. \]

b) Rate of hydrolysis of \([\text{Co(NH}_3)_5X]^2+\) is faster than \([\text{Co(PY}_3)_5X]^2+\). Comment.

c) Trans Ir (CO) Cl (PPh_3)_2 + CH_3I \rightarrow \ ?

Predict the product.

d) Explain the terms associative and dissociative reactions with examples.

e) Pick out the inert complexes.

\([\text{Cr(CN)}_6]^{3-}, [\text{Co(NH}_3)_6]^{3+}, [\text{Fe(H}_2\text{O)}_6]^{3+}. \]

Q2) Attempt any two of the following: [10]

a) Write note on ‘Ziegler Natta’ catalyst in polymerisation reaction.

b) Discuss the experimental evidences in conjugate base mechanism.

c) Give a brief account of Monsanto acetic acid process.

d) Explain the chelate effect in substitution cis octahedral complexes.
Q3) Answer any one of the following:

a) Determine valence shell electronic count.

i) \( \text{Fe}_2(\text{CO})_6 \).

ii) \( \text{(CO)}_5\text{Mn} - \text{Mn} - (\text{CO})_3 \).

iii) \( \eta^5 - \text{C}_5\text{H}_5 \text{)_2Fe} \).

iv) \( \eta^6 - \text{C}_6\text{H}_6 \text{)_2Cr} \).

v) \([\text{Co}_2(\text{CO})_8] \).

b) Discuss the role of NMR spectroscopy to predict structure of organometallic compounds.
Q1) Answer the following: [10]

a) Define: Triangular matrix with suitable example.

b) What is a multiple point and singular point on a curve?

c) If \( A = \begin{bmatrix} 2 & 1 & 4 \\ 5 & -3 & 7 \end{bmatrix} \)

\[ B = \begin{bmatrix} 1 & 2 & 3 \\ 2 & -4 & 6 \end{bmatrix} \] then find \( 2A - 3B \).

d) Differentiate the equation with respect to \( x \).

\[ y = \frac{2 + x}{2 - x} \]

e) If \( f(x) = x^2 + 5x + 5 \) then find values of \( f(0), f\left(\frac{1}{2}\right) \) and \( f(-1) \).
Q2) Attempt any two of the following: [10]

a) Solve the following equations using Cramer’s rule.
   \[ x + y + z = 7 \]
   \[ x + 2y + 3z = 16 \]
   \[ x + 3y + 4z = 22. \]

b) Solve \((y^2e^x + 2xy)dx - x^2dy = 0\) and state whether the equation is exact or not.

c) What is the maxima and minima of a function of single independent variable? Give the rules.

d) Evaluate the following:
   i) \[ \int (x^3 + x + 5) \, dx \]
   ii) \[ \int (x^2 - 3)^2 \, dx \]

Q3) Attempt any one of the following: [5]

a) Give equations and graphical representation for the following with suitable illustrations:
   i) Straight lines.
   ii) Slope and intercept.

b) Find the differential equation for the rate of the bimolecular reaction
   \[ A + B \rightarrow C \]
   where \( a \) and \( b \) are the original concentrations of \( A \) and \( B \) respectively and solve the differential equation.
Q1) Attempt any two of the following:          [8]

a) Draw the correlation diagram for DIS-rotatory opening of 1, 3
cyclohexadiene to 1, 3, 5-hexatriene and predict whether the reaction
will be thermally or photochemically allowed.

b) Explain the Mechanism of Free radical addition reaction of HBr to
propylene.

c) Discuss the Mechanism of Norrish type I process of 2, 2 - dimethyl
heptanone and predict the products formed.

Q2) Explain the mechanism for any three of the following:          [9]

a)  

b)  

c)  

13
Q3) A) Predict the products for Any two of the following indicating the mechanism involved

a) ![Chemical structure]

\[ H_2 \rightarrow ? \]

b) ![Chemical structure]

\[ \Delta \rightarrow ? \]

c) ![Chemical structure]

\[ \Delta \rightarrow ? + ? \]

d) ![Chemical structure]

\[ ? \]

B) Answer Any two of the following:

a) With the help of suitable example explain Claisen rearrangement.

b) Write a short note on Di-\(\Pi\) methane rearrangement.

c) Write a note on Jablonski diagram.