## Time : 3 Hours]

[Max. Marks: 80
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 indicates full marks.
4) Use of logarithmic table/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

## Physico - Chemical Constants

1. Avogadro Number
2. Boltzmann Constant
3. Planck Constant
4. Electronic Charge
5. 1 eV
6. Gas Constant
7. Faraday Constant
8. Speed of light
9. 1 cal
10. 1 amu
11. Bohr magneton
12. Nuclear magneton
13. Mass of an electron
$\mathrm{N}=6.022 \times 10^{23} \mathrm{~mol}^{-1}$
$\mathrm{k}=1.38 \times 10^{-16} \mathrm{erg} \mathrm{K} \mathrm{K}^{-1}$ molecule ${ }^{-1}$
$=1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ molecule ${ }^{-1}$
$\mathrm{h}=6.626 \times 10^{-27} \mathrm{erg} \mathrm{s}$
$=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
$\mathrm{e}=4.803 \times 10^{-10} \mathrm{esu}$
$=1.602 \times 10^{-19} \mathrm{C}$
$=23.06 \mathrm{k} \mathrm{cal} \mathrm{mol}^{-1}$
$=1.602 \times 10^{-12} \mathrm{erg}$
$=1.602 \times 10^{-19} \mathrm{~J}$
$=8065.5 \mathrm{~cm}^{-1}$
$R=8.314 \times 10^{7} \mathrm{erg} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$.
$=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$=1.987 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{F}=96487 \mathrm{C}^{\mathrm{equiv}}{ }^{-1}$
c $=2.997 \times 10^{10} \mathrm{~cm} \mathrm{~s}^{-1}$
$=2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
$=4.184 \times 10^{7} \mathrm{erg}$
$=4.184 \mathrm{~J}$
$=1.673 \times 10^{-27} \mathrm{~kg}$
$\beta_{e}=-9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$
$\beta_{n}=5.051 \times 10^{-27} \mathrm{~J} \mathrm{~T}^{-1}$
$m_{c}=911 \times 10^{-31} \mathrm{~kg}$.
P.T.O.

## SECTION - I

Q1) Attempt any three of the following:
a) What is an eigenfunction? How does a $Q$ class function differ from any other function?
b) Discuss Eienstein's photoelectric effect. How did it support Planck's hypothesis?
c) What is Bohr's correspondence principle? Prove $\frac{\mathrm{E}_{n+1}-\mathrm{E}_{n}}{\mathrm{E}_{n}}=\frac{2 n+1}{n^{2}}$.
d) State the inadequaacy of the $1^{\text {st }}$ law of thermodynamics. Hence state the second law.
e) Distinguish between state and path functions giving examples.

Q2) Attempt any three of the following:
a) What is Gibbs function? Explain its dependence on temperature.
b) Derive an expression for the change in entropy when two ideal gases are mixed.
c) What are azeotropes? How are they separated?
d) Derive the Gibbs Duhem equation and state its applications.
e) What is Clausins inequality? Explain its significance.

Q3) Attempt any two of the following:
a) Calculate the velocity of an electron ejected from a sodium surface $(\phi=1.82 \mathrm{eV})$ when light having frequency $1.13 \times 10^{15} \mathrm{~Hz}$ is incident on it.
b) When 5.25 g of a substance is dissolved in 565 g of benzene at $25^{\circ} \mathrm{C}$, the boiling point is raised by $0.625^{\circ} \mathrm{C}$. Evaluate the molecular weight of the substance. $\left[\mathrm{K}_{\mathrm{b}}=2.53 \mathrm{~K} \mathrm{Kg} \mathrm{mol}^{-1}\right]$.
c) The lifetime of an excited species is 2 ns . Determine the uncertainty in energy in SI units. How can the width of the spectral line be determined from this data?

Q4) Attempt any three of the following :
a) Derive the integral expression for a second-order rate law $\frac{d}{d t}[\mathrm{P}]=k[\mathrm{~A}][\mathrm{B}]$ for a reaction of a stoichiometry 2A $+3 \mathrm{~B} \rightarrow$ Product.
b) Discuss with suitable examples the phenomenon of chain reactions.
c) Using Bodenstein and Lind mechanism derive the rate equation for the formation of hydrogen bromide.
d) 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.
e) What is a fast reaction? Describe the relaxation method to study fast reactions.

Q5) Attempt any three of the following :
a) Discuss in detail the diffusion controlled limits. Write the equation relating diffusion - coefficient and flux of matter.
b) Explain the effect of ionic strength on the rate of a reaction.
c) Derive the expression for Bose - Einstein statistics and comment on the nature of the system for which the statistics is applicable.
d) Deduce the relationship between Gibbs energy and partition function.
e) Derive an expression for the rotational partition function and obtain the relation for standard entropy of a diatomic molecule.

Q6) Solve any two of the following :
a) A first order reaction has $\mathrm{K}=1.5 \times 10^{-6} \mathrm{~S}^{-1}$ at $200^{\circ} \mathrm{C}$. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed in the product? What is the half-life of this reaction?
b) Threshold energy of a reaction Ea is $15 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at 150 K . Calculate the percentage increase in the proportion of molecular collisions when temperature is increased by 15 K .
c) Calculate the ratio of the number of molecules in two energy levels at $27^{\circ} \mathrm{C}$, given that $\mathrm{E}_{2}=9.75 \times 10^{-3} \mathrm{erg} \mathrm{mol}^{-1}, \mathrm{E}_{1}=6.95 \times 10^{-13} \mathrm{erg} \mathrm{mol}^{-1}$, $\mathrm{g}_{1}=2$ and $\mathrm{g}_{2}=3$.

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## CH-130 : Molecular Symmetry and Chemistry of P-Block Elements (2008 Pattern) (Semester - I)

Time : 3 Hours]
[Max. Marks : 80
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 calculators is allowed.

## SECTION - I

Q1) Attempt any three of the following:
a) What are the conditions of mathematical group? Explain them using example of abelian group.
b) Classify the molecules $\qquad$ and $\qquad$ into appropriate point group.
c) Give general matrices for the following operations :
i) E
ii) i
iii) $\mathrm{C}_{2}^{z}$
iv) $\sigma^{x y}$
v) $S_{n}$.
d) Define and explain :
i) Proper axis of rotation.
ii) Centre of inversion.
e) Predict the products using cartesian coordinate system :
i) $\quad \mathrm{C}_{2}{ }^{7} \times \mathrm{C}_{2}{ }^{x}$
ii) $\quad \mathrm{C}_{2}{ }^{y} \cdot \sigma^{x z}$

Q2) Attempt any three of the following :
a) Draw all possible isomers of $\mathrm{Ma}_{2} \mathrm{~b}_{2} \mathrm{c}_{2}$. Explain on the basis of symmetry which of them is optically active?
b) Identify the point group and stereographic projections for :
i) $\mathrm{SOCl}_{2}$
ii) $\mathrm{H}_{2} \mathrm{~S}$.
c) Derive the character table for $\mathrm{C}_{2} \mathrm{~V}$ point group using orthogonality theorem.
d) Explain all symmetry elements of $\mathrm{SO}_{2} \mathrm{Cl}_{2}$ molecule and its point group.
e) Find out the normalized SALC for $\mathrm{NO}_{2}^{-}$ion, when projection operator $\mathrm{B}_{1}$ operates on $\phi_{1}$ orbital.

| $\mathrm{C}_{2} \mathrm{~V}$ | E | $\mathrm{C}_{2}^{z}$ | $\sigma_{v}{ }^{x z}$ | $\sigma_{v}{ }^{y z}$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{~B}_{1}$ | 1 | -1 | 1 | -1 |

Q3) Attempt any two of the following :
a) Using schematic symmetry operations show that for staggered ethane molecule, $\mathrm{S}_{n}{ }^{n}=\mathrm{E}$.
b) Sketch all symmetry operations of $\mathrm{NH}_{3}$ molecule.
c) Discuss the symmetry criterion for optically active molecules using suitable examples.
d) Using orthogonality theorem derive the character table for $\mathrm{H}_{2} \mathrm{O}_{2}$ molecule.

## SECTION - II

Q4) Attempt any three of the following:
a) What are interhalogen compounds? Give their important reactions giving balanced equations.
b) What are silicones? Give their preparation, properties and uses.
c) Give the classification of boron hydrides on the basis of skeletal electron pairs.
d) What is borazole \& why it is called as inorganic benzene? Give its reactions.
e) Give the allotropes of carbon. Draw the structure of graphite.

Q5) Attempt any three of the following :
a) Write short note on clatharate compounds of xenon.
b) Phosphanitrilic compounds - short note.
c) Write short note on 'Fullerene'.
d) Short note on Catenated and Cyclic Arsanes.
e) What are aluminosilicates?

Q6) a) Draw the structures of the following:
i) $\mathrm{N}_{2} \mathrm{O}_{4}$
ii) $\mathrm{IF}_{7}$
iii) $\mathrm{XeOF}_{4}$
iv) $\mathrm{B}_{3} \mathrm{~N}_{3} \mathrm{H}_{3} \mathrm{Cl}_{3}$
v) $\mathrm{P}_{4} \mathrm{O}_{10}$
b) Complete the following reactions:
i) $\mathrm{BX}_{3}+\mathrm{RNH}_{2} \rightarrow$ ?
ii) $\mathrm{S}_{8}+\mathrm{A}_{5} \mathrm{~F}_{5} \rightarrow$ ?
iii) $\mathrm{PCl}_{5}+\mathrm{nNH}_{4} \mathrm{Cl} \rightarrow ?+4 \mathrm{n} \mathrm{HCl}$
iv) $\left[\operatorname{Ir}\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{COCl}\right]+\mathrm{H}_{2} \rightarrow$ ?
v) $\mathrm{GeCl}_{4}+\mathrm{Al}_{2}(\mathrm{Me})_{6} \rightarrow$ ?
$\square$
P2760

ORGANIC CHEMISTRY

## CH-150 : Organic Reaction Mechanism and Stereochemistry (2008 Pattern) (Semester-I)

## Time : 3 Hours]

[Max. Marks : 80
Instructions to the candidates:

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

## SECTION-I

Q1) Explain any four of the following:
a) Salicyclic acid is 40 times stronger than P-hydroxy benzoic acid.
b) Chlorobenzene cannot be hydrolyzed using $\mathrm{SN}^{1}$ or $\mathrm{SN}^{2}$ conditions.
c) Neomenthyl chloride on treatment with sodium ethoxide in ethanol gives two products.
d) Cis 1, 3-dimethyl cyclohexane is unstable than cis 1, 4-dimethyl cyclohexane.
e) Tropylium bromide shows appreciable ionic character.

Q2) Write a short note on any three of the following:
a) Optical activity in biphenyls.
b) Regioselective reactions.
c) Ambident nucleophiles
d) Nucleophilicity and Basicity.

Q3) Predict the product/s with mechanism for any three of the following:
a)

b)

C)

d)


SECTION-II
Q4) Suggest the mechanism for any four of the following:
a)

b) -

i) $\mathrm{NH}_{2} \mathrm{NH}_{2}$
(i)


d)

e)



Q5) Attempt any four of the following:
a) Explain stability order of the following compounds.

b) Explain the aka values of the following compounds.

and


$$
P K_{a}=19.9
$$

$$
\text { PKG } 16.6
$$

c) Draw all possible conformational isomers of 1-ethyl-4-methyl cyclohexane.
d) 2, 6 di-t-butyl pyridine is less basic as compaired to Pyridine. Explain.
e) The proportion of quache conformation of 2-hydroxy ethane thiol is more than expected. Explain.

Q6) Attempt any eight of the following:
a) Assign $\mathrm{E} / \mathrm{Z}$ configuration of the following.

b) Assign pro $\mathrm{R} / \mathrm{S}$ of the following.

c) Assign $R / S$ configuration of the following.

d) Draw the resonance structures of the following.

e) Which of the following compound is optically active?

f) Identify aromatic, antiaromatic and non-aromatic of the following.

g) Explain factors affecting on the strength of acids.
h) Why tropone is more stable than anticipated?
i) Pyridine is more basic than Pyrrole. Explain.

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## PHYSICALCHEMISTRY

## CH-210 : Physical Chemistry - II

 (2008 Pattern) (Semester - II) (Old)
## Time : 3 Hours]

[Max. Marks: 80
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 indicates full marks.
4) Use of logarithmic table/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

## Physico-Chemical Constants

1. Avogadro Number
2. Boltzmann Constant
3. Planck Constant
4. Electronic Charge
5. 1 eV
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8. Speed of light
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13. Mass of an electron
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$=1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ molecule ${ }^{-1}$
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$=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
$\mathrm{e}=4.803 \times 10^{-10} \mathrm{esu}$
$=1.602 \times 10^{-19} \mathrm{C}$
$=23.06 \mathrm{k} \mathrm{cal} \mathrm{mol}^{-1}$
$=1.602 \times 10^{-12} \mathrm{erg}$
$=1.602 \times 10^{-19} \mathrm{~J}$
$=8065.5 \mathrm{~cm}^{-1}$
$\mathrm{R}=8.314 \times 10^{7} \mathrm{erg} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$.
$=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$=1.987 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{F}=96487 \mathrm{C}^{\mathrm{equiv}}{ }^{-1}$
c $=2.997 \times 10^{10} \mathrm{~cm} \mathrm{~s}^{-1}$
$=2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
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$\beta_{n}=5.051 \times 10^{-27} \mathrm{~J} \mathrm{~T}^{-1}$
$\mathrm{m}_{\mathrm{c}}=911 \times 10^{-31} \mathrm{~kg}$.
P.T.O.

## SECTION - I

Q1) Answer any three of the following :
a) Explain the hyperfine structure of ESR spectra.
b) Write a note on NMR spectroscopy principle.
c) Explain the advantages of FTIRS.
d) Write a note on Fortrat parabola.
e) Write an account of the quantum theory of Raman effect.

Q2) Answer any three of the following :
a) Explain the factors governing intensity of spectral lines.
b) What are overtones, fundamental lines and hot bands?
c) Deduce the relation $\mathrm{I}-\mathrm{\mu r}^{2}$ for a rigid molecule.
d) Explain the effect of nuclear spin or spectral spacings.
e) State and explain the Franck-Condon principle.

Q3) Solve any two of the following :
a) ${ }^{1} \mathrm{H}-{ }^{35} \mathrm{Cl}$ is irradiated with 436 nm line. Estimate the wave number of the first two anti Stokes lines.
b) Evaluate the spectral width for a line representing a transition to an excited state having a lifetime of 100 ps .
c) If B for a molecule is $0.36 \mathrm{~cm}^{-1}$, find $\mathrm{J}_{\text {max }}$ at $200^{\circ} \mathrm{C}$.

## SECTION - II

Q4) Attempt any three of the following:
a) Explain the terms G-value, electron absorption coefficient, spur and dead time.
b) Discuss the working of a scintillation counter. What is the role of pulse height analyzer in it?
c) What is hydrated electron? Give the different methods to obtain the hydrated electron.
d) Explain isotope separation method for plutonium.
e) What are the various modes of interaction of $\gamma$-rays with matter? Discuss any one of them in detail.

Q5) Attempt any three of the following:
a) Explain in detail critical size of thermal reactor.
b) What is the breeder reactor? Explain with an example the principle of breeding.
c) Describe the use of radioisotope in the measurement of the thickness of a moving sheet.
d) Explain how the concentration of an element in a sample is determined by NAA? What are disadvantages of this technique?
e) Draw and explain a radiometric titration curve where in the reagent is labelled.

Q6) Solve any two of the following:
a) The activity of a radioisotope fall to $1 / 12$ th of its initial value in 12 hours. Find its half-life and average life.
b) Find the thickness of lead required to reduce the level of radiation from $10,000 \mathrm{cpm}$ to $2,000 \mathrm{cpm}$. Given $\mu_{\mathrm{pb}}=0.57 \mathrm{~cm}^{-1}$.
c) A 0.1 g gun metal alloy containing $90 \% \mathrm{Cu}$ was irradiated for one day in a neutron flux $10^{9} \mathrm{ncm}^{-2} \mathrm{~S}^{-1}$. Calculate the activity after a cooling period of 6 hrs.
[Given : At. weight of $\mathrm{Cu}=63, t_{1 / 2}$ for ${ }^{64} \mathrm{Cu}=12.7 \mathrm{hrs}, \sigma=4.5$ barn and $\mathrm{r}=69.17 \%$ ]

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# CH - 250 : Synthetic Organic Chemistry \& Spectroscopy (2008 Pattern) (Semester - II) 

## Time : 3 Hours]

[Max. Marks: 80
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) Explain any four of the following:
a) Cyclohexene on treatment with m-CPBA followed by hydrolysis gives trans diol while treatment with $\mathrm{OsO}_{4}$ followed by hydrolysis gives cis diol.
b) In Baeyer-Villiger oxidation, t-butyl group migrates in preference to methyl group.
c) N-methyl benzamide doesn't undergo Backman rearrangement.
d) For synthesis of $\beta$-hydroxy ester, Reformatsky reaction is preferable than Grignard reaction.
e) Write the mechanism to convert alkene to alkane using Wilkinson's catalyst.

Q2) Write short note on any three of the following:
a) Claisen rearrangement.
b) Simon-Smith reaction.
c) Non-Classical carbocations.
d) Swern Oxidation.

Q3) Predict the product and suggest the mechanism for any four of the following.
a)


b)


a) HCl
c)

d)

e)


$$
\xrightarrow[\text { Dioxame } / \Delta]{\mathrm{SeO}_{2}} \text { ? }
$$

## SECTION - II

Q4) Suggest the mechanism for any four of the following.
a)

$\xrightarrow{\text { Peracid }}$

b)


c)

d)


e)



Q5) Attempt any four of the following:
a) Calculate $\lambda_{\text {max }}$ of the following compounds. Clearly show your calculations.


b) Arrange the following compounds according to the increasing carbonyl frequency. Justify.

(i)

(ii)

(iii)
c) Deduce the structure from the following spectral data.
M.F. $\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O} \quad \mathrm{UV}=240 \mathrm{~nm},-$ ve Iodoform test, IR peaks at $2720 \mathrm{~cm}^{-1} \& 1700 \mathrm{~cm}^{-1}$.
d) In Methyl salicylate carbonyl stretching frequency get shifted to lower end as compared to normal. Justify.
e) Explain the following:
i) Bathochromic shift
ii) Diamagnetic Anisotropy

Q6) Deduce the structure of any three of the following.
a) $\mathrm{MF}: \mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{2}$

PMR : $1.92 \delta(\mathrm{dd}, \mathrm{J}=1.6 \& 7.2 \mathrm{~Hz}, 12 \mathrm{~mm})$
5.86 ( $\mathrm{dq}, \mathrm{J}=1.6 \& 15.6 \mathrm{~Hz}, 4 \mathrm{~mm})$
$7.10 \delta(\mathrm{dq}, \mathrm{J}=6.9 \& 15.6 \mathrm{~Hz}, 4 \mathrm{~mm})$
$12.2 \delta$ (s, Exchangeable, 4 mm )
b) MF : $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{4} \mathrm{~N}$

IR : Broad band at $3450-3300,1710,1530,1350$ and $780 \mathrm{~cm}^{-1}$
PMR : $7.72 \delta(\mathrm{dd}, \mathrm{J}=7.7 \& 8.1 \mathrm{~Hz})$
$8.45 \delta(\mathrm{dt}, \mathrm{J}=1.5 \& 7.7 \mathrm{~Hz})$
$8.50 \delta(\mathrm{ddd}, \mathrm{J}=8.1 \mathrm{~Hz})$
$8.96 \delta(\mathrm{dd})$
$11.02 \delta$ (s, Exchangeable)
c) $\mathrm{MF}: \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NCl}_{2}$

IR : $3300-3400 \mathrm{~cm}^{-1}$
PMR : $5.10 \delta(\operatorname{Broad} \mathrm{~s}$, exchangeable, 2 H$)$
$7.23 \delta(\mathrm{~d}, \mathrm{~J}=2.3 \mathrm{~Hz}, 1 \mathrm{H})$

$$
7.02 \delta(\mathrm{dd}, \mathrm{~J}=2.3 \& 8.6 \mathrm{~Hz}, 1 \mathrm{H})
$$

$6.65 \delta(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 1 \mathrm{H})$
d) $\mathrm{MF}: \mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}$

IR : $1200-1280 \mathrm{~cm}^{-1}$
PMR : $1.32 \delta(\mathrm{~d}, \mathrm{~J}=6 \mathrm{~Hz}, 3 \mathrm{H})$
$2.42 \delta(\mathrm{dd}, \mathrm{J}=3.5 \& 2.5 \mathrm{~Hz}, 1 \mathrm{H})$
$2.72 \delta(\mathrm{dd}, \mathrm{J}=3.5 \& 3.0 \mathrm{~Hz}, 1 \mathrm{H})$
$2.98 \delta(\mathrm{ddq}, \mathrm{J}=2.5,3.0 \& 6 \mathrm{~Hz}, 1 \mathrm{H})$

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## Time : 3 Hours]

[Max. Marks: 80
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 indicates full marks.
4) Use of logarithmic table/calculator is allowed.
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$\beta_{e}=-9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$
$\beta_{n}=5.051 \times 10^{-27} \mathrm{JT}^{-1}$
$m_{e}=9.11 \times 10^{-31} \mathrm{~kg}$.

## SECTION - I

Q1) Attempt any four of the following :
a) The unnormalized wave function for a particle in a box is given by $\psi_{n}=\mathrm{A} \cdot \sin \frac{n \pi}{a} . x$

Normalize the wave function and determine the value of the normalization constant, A, for the limits $x=0$ and $x=a$.
b) Verify if $\frac{\hat{d}}{d x}$ and $\hat{x}$ commute on the function $f(x)$.
c) Explain what are regular and inverted multiplets.
d) Construct the total energy operator for
i) He atom and
ii) $\mathrm{H}_{2}^{-}$ions.

Explain the terms involved in each of these.
e) Obtain an expression for the first order connection to the energy of nondegenerate system according to the perturbation theory.
f) Discuss briefly a typical application of the variation method.

Q2) Attempt any four of the following:
a) What information does a term symbol give about the electron configuration? Find the terms corresponding to $\mathrm{d}^{2}$ state.
b) Obtain the HMO energies for naphthalene. What are the underlying assumptions?
c) Deduce the Huckel energies for cyclobutadiene. Why is the molecule not stable?
d) Discuss the $4 \mathrm{~m}+2$ rule of Huckel. Give examples.
e) Explain how Schaad modified Huckels method to determine orbital energies of molecules.
f) Distinguish between antiaromatic and aromatic compounds on the basis of REPE values.

## SECTION - II

Q3) Attempt any three of the following :
a) Discuss Einstein's specific heat theory of metals.
b) Derive $E_{0}=\frac{E_{c}+E_{v}}{2}$ for intrinsic semi-conductors.
c) Derive the expression for the number of Schottky defects present in a crystal at a given temperature.
d) Discuss briefly the mechanism of diffusion in solids.
e) Describe the methods of growing crystals from the vapour phase.

Q4) Attempt any three of the following:
a) Explain what are Ohmic and rectifying contacts in metal-semiconductor junctions.
b) Explain spin-spin and spin-lattice interactions in crystals.
c) Write a note on converse piezo electricity.
d) Explain the rate laws used to study the decelerations type of decompostion reactions in a single solid.
e) Write a note on 'Photographic process'.

Q5) Solve any two of the following:
a) Calculate the atomic specific heat of Al at $1 \mathrm{~K}\left[\theta_{\mathrm{D}}=398\right.$ for Al$]$.
b) The average energy required to produce a Frenkel defect in a crystal $\mathrm{A}^{2+}$ $\mathrm{B}^{2-}$ is 1.4 eV . Calculate the ratio of Frenkel defects at $20^{\circ} \mathrm{C}$ and $300^{\circ} \mathrm{C}$ in 1 g of the crystal.
c) Calculate the dislocation density in a crystal in which the total length of all the dislocations is 1 m and volume of the crystal is $1000 \mathrm{~mm}^{3}$.

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## PHYSICALCHEMISTRY

## CH-311 : Nuclear and Radiation Chemistry (New) (2008 Pattern) (Semester - III)

## Time : 3 Hours]

[Max. Marks: 80
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 indicates full marks.
4) Use of logarithmic table/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary:

## Physico-Chemical Constants

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

## SECTION - I

Q1) Attempt any three of the following:
a) Discuss the general aspects of nuclear reactor designing.
b) Explain the Kuroda's theory of nuclear fission in natural reactor.
c) Write a note on fission fragments and their mass distribution.
d) What are various types of nuclear fission? Explain any one of them.
e) Give an account of liquid drop model.

Q2) Attempt any three of the following:
a) What are the merits of collective model?
b) Draw the experimental setup for PIXE analysis.
c) Discuss the principle of RBS technique. What are its applications?
d) Describe how compound nucleus theory was verified experimentally?
e) Give an account of thermonuclear reaction.

Q3) Solve any two of the following:
a) What is the excitation energy of the compound nucleus resulting in the bombardment of ${ }^{27} \mathrm{Al}$ by $\alpha$ particles of energy 5 MeV on LS?

Given : mass is ${ }^{27} \mathrm{Al}=26.9815354$

$$
\begin{aligned}
& { }^{31} \mathrm{P}=30.9737634 \\
& \alpha=4.0026044
\end{aligned}
$$

b) In the fission of ${ }_{92}^{235} \mathrm{U}$ the end stable products are ${ }_{40}^{94} \mathrm{Zr}$ and ${ }_{55}^{140} \mathrm{Ce}$. What are the primary fragments?
c) Calculate the energies of the states a. $4(+)$, b. $6(+)$, c. $8(+)$ and d. $10(+)$; all being members of rotational band in an even. Even nucleus of which the eneroz of $2(+)$ state is 44 KeV .

## SECTION - II

Q4) Attempt any three of the following :
a) Discuss the working of $\mathrm{NaI}(\mathrm{T} l)$ scintilation counter. How gamma energy can be measured using this counter.
b) Describe the natural sources of radiation.
c) What are Prp's of water?
d) Discuss the mechanism of annealing.
e) Discuss Szilard chalmer reaction.

Q5) Attempt any three of the following :
a) Discuss the chemistry of recoil atom.
b) What are chemical and biological effects of radiation observed in a cell?
c) Discuss the internal radiation hazards.
d) Write note on $\mathrm{FeSO}_{4}-\mathrm{CuSO}_{4}$ dosimeter.
e) What are the causes of three miles nuclear accidents?

Q6) Attempt any two of the following :
a) ${ }^{60} \mathrm{Co}$ source exhibits dose rate $100 \mathrm{mrem} / \mathrm{h}$ at a distance one meter. At what distance from the source must a barrier be placed if the dose rate at the barrier becomes $25 \mathrm{mrem} / \mathrm{h}$ ?
b) The dose due to ${ }^{56} \mathrm{Mn}$ at a distance of 5 meter is $6 \mathrm{rem} / \mathrm{h}$. Find the strength of ${ }^{56} \mathrm{Mn}$ in millicurie. Given : ${ }^{56} \mathrm{Mn}$ emitts $\gamma$-rays of energy 847, 1811 and 2111 KeV .
c) Find the thickness of lead to reduce a dose due to $\gamma$-rays from $10 \mathrm{rad} / \mathrm{min}$ to $1 \mathrm{rad} / \mathrm{min}$. Given : $\mu_{\mathrm{Pb}}=0.7 \mathrm{~cm}^{-1}$.

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## PHYSICALCHEMISTRY

## CH-312 : Advanced Instrumental Methods of Analysis (2008 Pattern) (Semester-III) (New)

## Time : 3 Hours]

[Max. Marks: 80
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 br drawn WHEREVER necessary.

## Physico - Chemical Constants

1) Avogadro Number
2) Boltzmann Constant
3). Planck Constant
3) Electronic Charge
4) 1 eV
5) Gas Constant
6) Faraday Constant
7) Speed of light
8) 1 cal
9) $\operatorname{lamu}$
10) Bohr magneton
11) Nuclearmagneton
12) Mass of an electron
$\mathrm{N}=6.022 \times 1 \mathrm{c}^{23} \mathrm{~mol}^{-1}$
$\mathrm{k}=1.38 \times 10^{-18} \mathrm{erg} \mathrm{K}^{-1}$ molecule ${ }^{-1}$
$=1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ molecule ${ }^{-1}$
$\mathrm{h}=6.626 \times 10^{-27} \mathrm{erg} \mathrm{s}$
$=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
$\mathrm{e}=4.803 \times 10^{-10} \mathrm{esu}$
$=1.602 \times 10^{-19} \mathrm{C}$
$=23.06 \mathrm{k} \mathrm{cal} \mathrm{mol}^{-1}$
$=1.602 \times 10^{-12} \mathrm{erg}$
$=1.602^{-1} \times 10^{-19} \mathrm{~J}$
$=8065.5 \mathrm{~cm}^{-1}$
$\mathrm{R}=8.314 \times 10^{7} \mathrm{ergK}^{-1} \mathrm{~mol}^{-1}$
$=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$=1.987 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{F}=96487 \mathrm{C}_{\text {equiv }}{ }^{-1}$
c $=2.997 \times 10^{10} \mathrm{~cm} \mathrm{~s}^{-1}$
$=2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
$=4,184 \times 10^{7} \mathrm{erg}$
$=4.184 \mathrm{~J}$
$=1.673 \times 10^{-27} \mathrm{~kg}$
$\beta_{e}=-9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$
$\beta_{\mathrm{n}}=5.051 \times 10^{-27} \mathrm{~J} \mathrm{~T}^{-1}$
$\mathrm{m}_{\mathrm{c}}=9.11 \times 10^{-31} \mathrm{~kg}$

## SECTION-I

Q1) Attempt any three of the following:
a) Define the terms: matrix, cross-section, sensitivity target and flux.
b) Explain the terms excitation function and saturation activity in activation analysis.
c) What are the limitations of neutron activation analysis technique?
d) Describe are and spark ionization method used in mass spectrometry.
e) Draw a neat labelled diagram of time-of-flight analyzer and explain its working.

Q2) Attempt any three of the following:
a) Discuss the gas-phase chemiluminescent analysis with a typical example.
b) Explain the mechanism of electrochemiluminescence.
c) State the principle of X-ray fluorescence. Draw a neat labelled diagram of wavelength-dispersive X-ray fluorometer.
d) Describe with a neat labelled diagram the apparatus for fluorescence.
e) Write a note on scanning electron microscope (SEM).

Q3) Attempt any two of the following:
a) Calculate the mass absorptive coefficient of an alloy which consists of 27 percent nickel and 73 percent copper at the wavelength corresponding to $\mathrm{K}_{\alpha}$ radiation of copper. The mass absorptive coefficient at that wavelength is $49.3 \mathrm{~cm}^{2} / \mathrm{g}$ for nickel and $52.7 \mathrm{~cm}^{2} / \mathrm{g}$ for copper.
b) What accelerating potential is required to focus an ion with $\mathrm{m} / \mathrm{z} 348$ on the entrance slit of a detector if the radius of curvature of the magnetic analyzer and applied flux density are 21.2 cm and 1.00 T respectively.
c) 0.8 gm of an alloy containing $1.5 \%$ tungsten was irradiated in a neutron flux of $2 \times 10^{7} \mathrm{n} \mathrm{cm}^{-2} \mathrm{~s}^{-1}$ for 24 h . Find out the activity of sample in dpm. (Given : $\gamma=28.6 \%, \sigma=37.86$ barn, $\mathrm{t}_{1 / 2}$ of ${ }^{187} \mathrm{~W}=23.8 \mathrm{hr}$ ).

## SECTION-II

Q4) Attempt any three of the following:
a) With a neat labelled diagram, describe the working of a typical ICP-emission spectrometer.
b) Describe the technique of sample introduction into the ICP in ICP-AES.
c) Briefly, describe the applications of thermogravimetry.
d) State the principle of thermometric titrations. Describe a typical thermometric titration curve.
e) Discuss the mechanism by which satellite peaks are observed in ESCA.

Q5) Attempt any three of the following:
a) Enlist the advantages of coulometric titrations.
b) Write a note on ESCA chemical shift.
c) With a neat labelled diagram, describe the analysis by controlled-potential coulometry technique.
d) What is hydrodynamic voltammetry? Describe the electrodes used in the technique.
e) Give a brief account of pulse-voltammetry.

Q6) Solve any two of the following:
a) The initial current is 90 mA and it decreases exponentially with $\mathrm{k}=0.0058 \mathrm{sec}^{-1}$, the titration time $=714 \mathrm{sec}$. How many milligrams of Uranium (VI) are reduced to Uranium (IV)?
[At. Wt. of $\mathrm{U}(\mathrm{VI})=238$ ]
b) A 25.0 ml portion of a solution containing ethylenediamine was thermometrically titrated with 1.046 M hydrochloric acid.

$$
\mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}+\mathrm{HCl} \rightarrow \mathrm{H}_{2} \mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{3}^{+}+\mathrm{Cl}^{-}
$$

The first end point of the titrations was 1.048 ml . Determine the concentration of ethylenediamine in the solution.
c) In an ESCA experiment, Cr k $\alpha$ X-rays $(\lambda=2.294)$ caused the ejection of electrons from a calcium compound. The measured kinetic energy was 1.201 kev and the work function was 3.4 eV . Calculate the binding energy for these electrons in the calcium atom.

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M.Sc.

## PHYSICALCHEMISTRY

## CH-314 : Polymer Chemistry (2008 Pattern) (Semester-III) (New)

Time : 3 Hours]
[Max. Marks : 80
Instructions to the candidates:

1) Asnwers 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
2) Boltzmann Constant
3). Planck Constant
3) Electronic Charge
4) 1 eV
5) Gas Constant
6) Faraday Constant
7) Speed of light
8) 1 cal
9) $1 a m u$
10) Bohr magneton
11) Nuclear magneton
12) Mass of an electron

$$
\begin{aligned}
\mathrm{N} & =6.022 \times 1 \mathrm{C}^{23} \mathrm{~mol}^{-1} \\
\mathrm{k} & =1.38 \times 10^{-16} \mathrm{erg} \mathrm{~K}^{-1} \text { molecule }{ }^{-1} \\
& =1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1} \text { molecule }{ }^{-1} \\
\mathrm{~h} & =6.626 \times 10^{-27} \mathrm{erg} \mathrm{~s}^{2} \\
& =6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s} \\
\mathrm{e} & =4.803 \times 10^{-10} \mathrm{esu} \\
& =1.602 \times 10^{-19} \mathrm{C} \\
& =23.06 \mathrm{k} \mathrm{cal} \mathrm{~mol} \\
& =1.602 \times 10^{-12} \mathrm{erg}^{-1} \\
& =1.602 \times 10^{-19} \mathrm{~J} \\
& =8065.5 \mathrm{~cm}^{-1} \\
\mathrm{R} & =8.314 \times 10^{7} \mathrm{ergK}^{-1} \mathrm{~mol}^{-1} \\
& =8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \\
& =1.987 \mathrm{cal} \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \\
\mathrm{~F} & =96487 \mathrm{Cequiv}^{-1} \\
\mathrm{c} & =2.997 \times 10^{10} \mathrm{~cm} \mathrm{~s}^{-1} \\
& =2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1} \\
& =4.184 \times 10^{7} \mathrm{erg}^{2} \\
& =4.184 \mathrm{~J} \\
& =1.673 \times 10^{-27} \mathrm{~kg}^{2} \\
\beta_{\mathrm{e}} & =-9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T} \\
\beta_{\mathrm{m}} & =5.051 \times 10^{-27} \mathrm{~J} \mathrm{~T} \\
\mathrm{~m}_{\mathrm{c}} & =9.11 \times 10^{-31} \mathrm{~kg}^{2}
\end{aligned}
$$

Q1) Attempt any three of the following:
a) Discuss classification of polymers based on
i) Origin
ii) Atoms in the main chain with the suitable examples.
b) Deduce expression for enthalpy, entropy and free energy of mixing of polymer solutions.
c) Discuss the flory-krigbaum theory for dilute polymer solutions.
d) What is Copolymer? Derive the Copolymer equation.
e) What are reactivity ratios? Give the different conditions for obtaining different types of co-polymers.

Q2) Attempt any three of the following:
a) Explain the phenomena of viscous flow for polymers.
b) On which factor the glass transition temperature depends? Explain.
c) Why does polypropylene undergo a greater change in physical properties near $\mathrm{T}_{\mathrm{g}}$ than does linear polyethylene?
d) Why crystaline melting point of polyamide are greater than comparable polyesters.
e) Discuss the mechanical properties of crystalline polymers.

Q3) Solve any two of the following:
a) 1 mole of butadiene is copolymerised with 4 moles of Vinyl chloride the monomer reactivity ratios are 8.8 and 0.035 respectively. Calculate the instantaneous composition of polymer formed.
b) The following viscosity data were obtained for a sample of cellulose acetate in acetone at $25^{\circ} \mathrm{C}$.

| $\mathrm{C}(\mathrm{g} / 100 \mathrm{ml})$ | 0 | 0.114 | 0.351 | 0.703 |
| :--- | :--- | :--- | :--- | :--- |
| $\eta($ millipoise $)$ | 3.16 | 4.06 | 6.64 | 13.02 |
| $\mathrm{k}=1.87 \times 10^{-5} \mathrm{dl} / \mathrm{g}, \alpha=1.03$. | Calculate $\overline{\mathrm{M}}_{\mathrm{V}}$. |  |  |  |

c) Calculate the free energy of mixing of 50 gm of polystyrene of molecular weight $2 \times 10^{5}$ in 1 kg of benzene. Take $x_{1}=0.23$ and assuming no change in density.

## SECTION-II

Q4) Attempt any three of the following:
a) Describe preparation of polymer sample for IR and explain applications of IR spectroscopy for crystallinity in polymers.
b) Explain vapour phase osmometry to determine the molecular weight of polymers.
c) Give an account of wet spinning process.
d) What are fillers? Explain their reinforcement in polymers.
e) Describe the method of end group analysis used to determine molecular weight of polymer.

Q5) Attempt any three of the following:
a) What is TGA? Explain how thermal stability of polymer can be assessed using this technique.
b) Give applications of conducting polymers.
c) Discuss the use of polymer exposure for
i) Polymer modification.
ii) Preparation of graft polymers.
d) Why it is necessary to express the molecular weight of a polymer sample as some average or molecular weight. Define $\overline{\mathrm{M}}_{v}, \overline{\mathrm{M}}_{n}$ and $\overline{\mathrm{M}}_{v}$.
e) Explain melt-spinning with neat labelled diagram.

Q6) Solve any two of the following:
a) Sedimentation equilibrium suspension of congored gives the following data.
initial concentration $0.1 \mathrm{gm} / \mathrm{L}$
rotor speed 299.6 rps

$$
\begin{array}{ll}
\bar{v}=0.60 & \mathrm{P}=1.00 \\
\text { at } \mathrm{X}_{2}=5.75 \mathrm{~cm} & \mathrm{C}_{2}=42.18 \mu \\
\text { at } \mathrm{X}_{1}=5.72 \mathrm{~cm} & \mathrm{C}_{1}=39.76 \mu
\end{array}
$$

Calculate the molecular weight.
b) State giving reasons, the type of copolymer formed when monomers have following reactivity ratios.

|  | $\mathrm{r}_{1}$ | $\mathrm{r}_{2}$ |
| :--- | :--- | :--- |
| Case I | 0.02 | 0.01 |
| Case II | 55.0 | 0.01 |

c) Evaluate $\overline{\mathrm{M}}_{n}, \overline{\mathrm{M}}_{w}$ and polydispersity index ratio for mixture of four molecules, each having the molecular weights as $1.25 \times 10^{6}, 1.50 \times 10^{6}$, $1.75 \times 10^{6}$ and $2.0 \times 10^{6}$.

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## PHYSICALCHEMISTRY

## CH-315 :Special Topics in Physical Chemistry (2008 Pattern) (Semester-III) (New)

## Time : 3 Hours]

[Max. Marks : 80
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
2) Boltzmann Constant
3). Planck Constant
3) Electronic Charge
4) 1 eV
5) Gas Constant
6) Faraday Constant
7) Speed of light
8) 1 cal
9) 1 amu
10) Bohr magneton
11) Nuclearmagneton
12) Mass of an electron
$\mathrm{N}=6.022 \times 1 \mathrm{C}^{23} \mathrm{~mol}^{-1}$
$\mathrm{k}=1.38 \times 10^{-16} \mathrm{erg} \mathrm{K}^{-1}$ molecule ${ }^{-1}$
$=1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ molecule ${ }^{-1}$
$\mathrm{h}=6.626 \times 10^{-27} \mathrm{erg} \mathrm{s}$
$=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
$\mathrm{e}=4.803 \times 10^{-10} \mathrm{esu}$
$=1.602 \times 10^{-19} \mathrm{C}$
$=23.06 \mathrm{k} \mathrm{cal} \mathrm{mol}^{-1}$
$=1.602 \times 10^{-12} \mathrm{erg}$
$=1.602^{-} \times 10^{-19} \mathrm{~J}$
$=8065.5 \mathrm{~cm}^{-1}$
$\mathrm{R}=8.314 \times 10^{7} \mathrm{ergK}^{-1} \mathrm{~mol}^{-1}$
$=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$=1.987 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{F}=96487 \mathrm{C}_{\mathrm{equiv}}{ }^{-1}$
c $=2.997 \times 10^{10} \mathrm{~cm} \mathrm{~s}^{-1}$
$=2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}$
$=4.184 \times 10^{7} \mathrm{erg}$
$=4.184 \mathrm{~J}$
$=1.673 \times 10^{-27} \mathrm{~kg}$
$\beta_{e}=-9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$
$\beta_{\mathrm{n}}=5.051 \times 10^{-27} \mathrm{~J} \mathrm{~T}^{-1}$
$\mathrm{m}_{\mathrm{c}}=9.11 \times 10^{-31} \mathrm{~kg}$

## SECTION-I

Q1) Attempt any four of the following:
a) State the types of sensors with their requirements.
b) Classify sensors according to the type of output signals and materials used.
c) Write a proton condition for $\mathrm{Na}_{2} \mathrm{C}_{2} \mathrm{O}_{4}$ and $\mathrm{H}_{2} \mathrm{~S}$.
d) Write mass balance on sodium and selenide in $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{Se}$ and charge balance for NaCN .
e) Give general applications of various structural properties of ceramics.
f) Discuss the phenomenon of catalysis in concentrated strong acid solutions.

Q2) Attempt any four of the following:
a) Draw a logarithmic concentration diagram for $0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{CO}_{3}$. (Given : $\mathrm{pka}_{1}=6.35, \mathrm{pka}_{2}=10.25$ )
b) The pH of a 0.1 M solution of a salt of phosphoric acid is 12.49 . Find the fractions of phosphoric acid existing as $\mathrm{H}_{3} \mathrm{PO}_{4}, \mathrm{H}_{2} \mathrm{PO}_{4}^{-}, \mathrm{HPO}_{4}^{2-}$ and $\mathrm{PO}_{4}^{3-}$ in the solution.
(Given : $\mathrm{ka}_{1}=5.9 \times 10^{-3}, \mathrm{ka}_{2}=6.15 \times 10^{-8}, \mathrm{ka}_{3}=4.8 \times 10^{-13}$ )
c) What is the influence of the surrounding gas atmosphere on the properties of semiconductor porous ceramics?
d) Calculate the pH and concentration of all ionic species in 0.1 N $\mathrm{CH}_{3} \mathrm{COOH}$ (Given: $\mathrm{ka}=1.85 \times 10^{-5}$ ).
e) Write the mechanism of the phenol-acetone condensation reaction to give bisphenol A.
f) Define the terms; activity, inhibitor, poison, specific and general acid catalysis as used in catalysis.

## SECTION-II

Q3) Attempt any four of the following:
a) Write a note on under water actuation.
b) Briefly explain the term "rubber like ceramics".
c) Describe the characteristics of
i) Smart car
ii) Smart window
d) Discuss the working of scanning tunneling microscope.
e) What are the limitations of phase rule?
f) Explain "azeotropic mixtures".

Q4) Attempt any four of the following:
a) What are nanomachines? Explain it.
b) Write a note on Fulerines.
c) State the characteristics of Passive smartness.
d) Comment on -Smart materials will bring revolution in human life.
e) Discuss the phase diagram of phenol-water system.
f) Discuss the effect of added salt in phase diagram of two component partially miscible system.

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$\square$
M.Sc. - II

INORGANIC CHEMISTRY
CH-326 : Organometallic Compounds of Transition Metals and Homogeneous Catalysis
(2008 Pattern) (Semester-III)

## Time : 3 Hours]

[Max. Marks: 80
Instructions to the candidates:

1) All questions are compulsory and carry equal marks.
2) Figures to the right indicates full marks.
3) At.No. $V=23, M n=25, F e=26 R h=45, W=74$.

Q1) Attempt any FOUR of the following:
a) State the EAN rule and calculate ' $n$ ' value of the following compounds.
i) $\quad\left(\eta^{5} \mathrm{C}_{5} \mathrm{H}_{5}\right) \mathrm{V}(\mathrm{CO})_{\mathrm{n}}$
ii) $\mathrm{Na}_{2} \mathrm{Fe}(\mathrm{CO})_{\mathrm{n}}$
iii) $\operatorname{MnBr}(\mathrm{CO})_{n}$
iv) $\left(\eta^{5} \mathrm{C}_{5} \mathrm{H}_{5}\right) \mathrm{Rh}(\mathrm{CO})_{\mathrm{n}}$
v) $\left(\eta^{6} \mathrm{C}_{6} \mathrm{H}_{6}\right) \mathrm{W}(\mathrm{CO})_{\mathrm{n}}$
b) Give the different methods for the preparation of metal-carbonyl compounds.
c) Explain the utility of OMC's in agriculture and horticulture.
d) What do you mean by hydrocyanation reaction? Which catalysts are used for the reaction. Explain with one example.
e) Explain the typical reactions of $\mathrm{TiCl}_{2}\left(\eta^{5} \mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$.

Q2) Attempt any FOUR of the following:
a) What haptacities are possible for the following ligands.
i) $\mathrm{C}_{2} \mathrm{H}_{4}$
ii) Cyclopentadienyl
iii) $\mathrm{C}_{6} \mathrm{H}_{6}$
iv) Butadiene
v) Cyclo octatetraene
b) What do you understand by -
i) Sand wich compounds?
ii) Bent metallocene. Describe the methods of synthesis of metallocene.
c) Explain the difference in IR spectra of the following:
i) $\mathrm{Mo}\left(\mathrm{PF}_{3}\right)_{3} \mathrm{CO}_{3} \mathrm{Vs} \mathrm{Mo}\left(\mathrm{PMe}_{3}\right)_{3} \mathrm{CO}_{3}$
ii) $\mathrm{MnCp}(\mathrm{CO})_{3} \mathrm{Vs} \mathrm{MnCp}^{*}(\mathrm{CO})_{3}$
d) Discuss mechanism of hydroformylation reaction of alkene with rhodium and cobalt catalysis.
e) Give a brief account of the preparative methods and properties of metalnitrosyl compounds.

Q3) Attempt any FOUR of the following:
a) Explain the $\mathrm{V}(\mathrm{CO})$ band in the IR spectrum of $\left[\mathrm{Fe}(\mathrm{CO})_{4}\right]^{-2}$ is at about $1790 \mathrm{~cm}^{-1}$, where as for $\mathrm{Ni}(\mathrm{CO})_{4}$ it is about $2060 \mathrm{~cm}^{-1}$.
b) Discuss in detail production of aldehydes with wacker's process.
c) Give the systematic classification of $\sigma$ - bonded T.M. hydrocarbyls.
d) Comment on the therapeutic properties of -
i) Mercurochrome
ii) Salvarsan
iii) Silatrane and
iv) Cisplatin
e) What do you mean by Heck reaction? Explain the steps involved in cyclopropanation reaction.

Q4) Write short notes any FOUR:
a) Fluxional behaviour of organometallics.
b) Tolman's catalytic cycle.
c) Group V OMC's in medicine.
d) Metal arene compounds.
e) Pianostool compounds.

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$\square$

## Time : 3 Hours]

[Max. Marks: 80

## Instructions to the candidates:

1) All questions are compulsory and carry equal marks.
2) Neat diagrams must be drawn wherever necessary.
3) Use of logarithmic table and calculator is allowed.

Q1) Attempt any four of the following:
a) What are the basic assumptions of CFT? Discuss the crystal field splitting of an octahedral and square planar complex.
b) Explain the terms :
i) Antiferromagnetic material.
ii) Solute - solute interaction.
c) Predict the type of magnetic exchange which occurs via the $90^{\circ}$ exchange pathway in the systems $d^{1}-d^{1}, d^{2}-d^{2}, d^{3}-d^{3}, d^{8}-d^{8}$ and $d^{9}-d^{9}$.
d) Give the characteristic properties of diamagnetic, paramagnetic and Ferromagnetic substances.
e) Explain the experimental magnetic moment of the following ions.
$\mathrm{Mn}^{3+} \mu$ B.m. expt $=\sim 4.9$ B.m.
$\mathrm{Co}^{2+} \mu$ B.m. expt $=\sim 4.1$ to 5.2 B.m.
(Given : Atomic no. of $\mathrm{Mn}=25$ and that of $\mathrm{Co}=27$ )

Q2) Attempt any four of the following:
a) Discuss the various models to account for the anomalous magnetic behaviour of transition metal complexes.
b) Explain the terms :
i) Canting.
ii) Spin pairing.
c) Write a note on Magnetically dilute and concentrated systems.
d) Discuss the effect of $\pi$-bonding on the value of $\Delta$ in an octahedral complex with the ligands capable of forming the $\pi$-bond.
e) $\mathrm{Mn}_{2}(\mathrm{CO})_{10}$ is diamagnetic. Explain.

Q3) Attempt any four of the following :
a) Discuss the mechanism of electron transfer reaction with reference to outer sphere reactions.
b) Explain the mechanism of photographic process.
c) Discuss in brief isomerisation of octahedral complexes.
d) Write a note on complementary and non-complementry reactions.
e) Explain the role of solvent in substitution reaction of square planar complexes.

Q4) Attempt any four of the following :
a) With the help of 'trans effect' how would you synthesize cis-chloroiodobis (pyridine) platinum (II) from $\mathrm{K}_{2} \mathrm{P}+\mathrm{Cl}_{4}$ ?
b) Write a note on Anation reactions.
c) Explain the main reaction types with suitable examples.
d) Discuss in brief oxidative addition reactions.
e) Write a note on Base Hydrolysis.

$\square$

## CH-331 : Structural Methods in Inorganic Chemistry (2008 Pattern) (Semester - III)

## Time : 3 Hours]

[Max. Marks : 80

## Instructions to the candidates:

1) All questions are compulsory.
2) All questions carry equal marks.
3) Use of calculator's is allowed.

Q1) Answer the following (any four) :
a) Draw the Mössbauer spectra for the product formed between $\mathrm{FeCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ with $\mathrm{K}_{4}\left[\mathrm{Fe}(\mathrm{CH})_{6}\right]$.
b) Explain the ESR - spectra for t-butyl radical.
c) Explain the ${ }^{31} \mathrm{P}-\mathrm{NMR}$ spectra of $\left[\mathrm{Cr}\left(\mathrm{POCH}_{3}\right)_{3}(\mathrm{CO})_{3}\right]^{3+}$ and draw the isomer of these molecule.
d) Explain the instrumentation of cyclic voltammetry.
e) Explain the types of nuclei in NQR spectrascopy. Which nuclei is NQR active and why?

Q2) Answer the following (any four):
a) What is XPS? Explain the XPS required UHV condition.
b) What is the principle of SEM? Explain the working of SEM.
c) What is DTA? Explain the instrumentation and working of DTA.
d) Explain the Bragg's law for determination of Crystal system.
e) What is meant by $9_{\perp \perp}$ and $9_{\perp}$ ? Explain the G.

Q3) Answer the following (any four):
a) Explain the Mössbauer spectrum for $\mathrm{Fe}(\mathrm{CO})_{5}$ at liquid nitrogen temperature.
b) What are Miller indices? Compute the Miller indices for faces having intercepts.
i) $\left[\frac{1}{2} 1 \frac{1}{2}\right]$
ii) $\left[\begin{array}{lll}1 & 0 & 0\end{array}\right]$
iii) $\left[\frac{1}{2} \frac{1}{2} \frac{1}{2}\right]$
c) Calculate the percentage of $\mathrm{MgCO}_{3}$ and $\mathrm{CaCO}_{3}$ in 40 mg of limestone sample that exhibits thermorgram showing weight of 30 mg at $500^{\circ} \mathrm{C}$ and 18 mg at $900^{\circ} \mathrm{C}$.
(Given - At. Wt. $\mathrm{Ca}=40.08, \mathrm{Mg}=24.31, \mathrm{C}=12.01, \mathrm{O}=15.99$ )
d) Draw the ${ }^{19} \mathrm{~F}$ - NMR spectra for $\mathrm{BF}_{3}$ molecule considering the natural abundance of $\mathrm{B}^{10}(\mathrm{I}=3)$ and $\mathrm{B}^{11}(\mathrm{I}=3 / 2)$ isotopes of boron.
e) Calculate NQR-transition frequencies for nucleus having spin quantum no. $I=3 / 2$. Assuming
i) $\quad \eta=0$
ii) $\quad \eta \neq 0$

Q4) Write short notes on (Any four) :
a) Factors affecting DTA curve.
b) TEM.
c) Hyperfine and superhyperfine splitting in ESR.
d) Instrumentation of DSC.
e) Differentiate between ${ }^{19} \mathrm{~F}-\mathrm{NMR}$ and ${ }^{31} \mathrm{P}-\mathrm{NMR}$ spectroscopy.

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$\square$INORGANIC CHEMISTRYCH-332 : Bio-Inorganic Chemistry : Inorganic Elements in theChemistry of Life
(2008 Pattern) (Semester - III)

## Time : 3 Hours]

[Max. Marks: 80
Instructions to the candidates:

1) All questions are compulsory.
2) All questions carry equal marks.
3) Neat diagrams must be drawn wherever necessary.

## Q1) Answer the following (Any four):

a) Why small molecular models for the active site structures of metallo enzymes are studied?
b) Give comparitive account of Type I, Type II and Type III copper proteins with suitable examples.
c) Differentiate between oxidative and hydrolytic cleavage of DNA.
d) Comment on 'why nature has chosen $\mathrm{Zn}^{2+}$ instead of $\mathrm{CO}^{2+}$ in the natural hydrolases'.
e) With appropriate diagrams, discuss the properties of the species formed during homolytic and heterolytic cleavage of $\mathrm{Co}-\mathrm{C}$ bond in vitamin $\mathrm{B}_{12}$.

Q2) Attempt any four of the following:
a) Why auranofin is better than solganol or myocrysin in the treatment of rheumatoid arthritis?
b) Draw the structures and explain the differences between porphyrin, chlorin and corrin ring systems.
c) Name the enzymes containing copper at their active site. Describe in brief the structure and function of $\mathrm{Cu}-\mathrm{Zn} \mathrm{SOD}$.
d) Explain the structure and function of enzyme urease.
e) Discuss the role of manganese in enzyme peroxidase.

Q3) Answer the following (Any four):
a) With the help of suitable examples explain oxidative cleavage of DNA by transition metal complexes.
b) What are unique structural features of the enzyme xanthene oxidase?
c) Explain in brief the biomethylation reaction catalysed by vitamin $\mathrm{B}_{12}$.
d) Why ${ }^{99 \mathrm{~m}} \mathrm{Tc}$ complexes are used in radiopharmaceuticals? Give two examples of non-technetium radiopharmaceuticals..
e) Which compounds are used in magnetic resonance imaging? Explain their properties.

Q4) Write short notes on (Any four):
a) Photosystem II.
b) Carbonic anhydrase.
c) DNA intercalation.
d) Nitrate oxidase.
e) Azurin.

## $\rightarrow \rightarrow \rightarrow$

$\square$

ORGANIC CHEMISTRY

## Time : 3 Hours]

[Max. Marks: 80

## Instructions to the candidates:

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

## SECTION - I

Q1) Attempt any four of the following :
a) Predict the sign of Hammett. Constants for $\mathrm{P}-\mathrm{OCH}_{3}, \mathrm{p}-\mathrm{NMe}_{3}, \mathrm{~m}-\mathrm{OH}$ and $\mathrm{m}-\mathrm{NO}_{2}$.
b) Discuss thermodynamics implications of linear free energy relationship.
c) Give evidences to support neighbouring group participation.
d) Which of the following prefers error form?

and

e) Predict the PKa for the following phenols using the appropriate substituent constants, a PKa for unsubstituted phenol is 9.90 and a $\rho$ - value of 2.25 .


Q2) Write short notes on any three of the following :
a) Benzoin condensation.
b) Reaction rate and free energy of activation.
c) Curtius rearrangement.
d) Acyloin condensation.

Q3) Predict the product with mechanism (Any four) :
a) PhCOCOOH

$?$
NAD
b)
 $\xrightarrow{h v}$ $?$
c)


d)


AcOH
$\longrightarrow \quad 9$.
e)


## SECTION - II

Q4) Explain any four of the following:
a) n-butyl bromide reacts slowly than
b) The Wolff rearrangement with suitable example.
c) The reduction of carboxyl function with NADH.
d) The uses of carbenes with proper examples.
e) The Claisen-Schmidt condensation reaction with suitable example.

Q5) Suggest the mechanism (Any four):
a)


b) Acetone

c)



d) $\quad \mathrm{PhCHO}+\mathrm{AC}_{2} \mathrm{O} \xrightarrow[D]{\mathrm{NaOAC}} \quad \mathrm{Ph}-\mathrm{CH}=\mathrm{CH}-\mathrm{COO} 7$ 2. $\mathrm{H}_{3} \mathrm{O}^{+}$
e)


」.



$$
2
$$

$$
\mathrm{N}_{2} \mathrm{OS}
$$

$$
\text { 3. } \mathrm{H}_{3} \mathrm{O}^{+}
$$

Q6) Answer any four of the following:
a) Which factors stabilize carbanions?
b) Substituent at $\beta$-position reduces the rate of AAC 2 mechanism.
c) Explain any reaction which involves nitrene intermediate.
d) Explain the nature's error equivalent.
e) Explain the Favorskii rearrangement with an example.

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$\square$

## CH-351 : Spectroscopic Methods in Structure Determination (2008 Pattern) (Semester - III)

## Time : 3 Hours]

[Max. Marks : 80
Instructions to the candidates:

1) All questions are compulsory.
2) Figures to the right indicate maximum marks.
3) Answers to the two sections to be written in separate answer books.
4) Spectroscopic data tables are not provided.

## SECTION - I

Q1) Explain any four of the following:
a) The ${ }^{1} \mathrm{H}$ spectrum of 2-hydroxy-5-isopropyl-2-methylcyclohexanone below has a ${ }^{3} \mathrm{~J}_{56}=3 \mathrm{~Hz}$ in benzene $-\mathrm{d}_{6}$ but $11 \mathrm{H}_{2}$ in $\mathrm{CD}_{3} \mathrm{OD}$.

b) A trisubstituted benzene possessing one bromine and two methoxy substituents exhibits three aromatic signals at $\delta 6.40,6.46$ and 7.41. Write the possible substitution pattern and justify.
c) 1-hexanol shows a base peak at $\frac{m}{e} 56$ while 2 -hexanol at $\frac{m}{e} 45$ and 2-methyl-2-pentanol at $\frac{m}{e} 59$.
d) Factors affecting chemical shifts in CMR.
e) Benefits of MALDI-TOF over EI-MS.

Q2) Answer any four of the following :
a) Two isomeric ketones with M.F. $\mathrm{C}_{7} \mathrm{H}_{14} \mathrm{O}$ show the following CMR \& PMR signals. Assign the structures to them based upon the data provided.
i) $\quad \mathrm{CMR}: \delta \quad 14,18,44,209$.

PMR : $\delta \quad 0.9 \mathrm{t}, 15 \mathrm{~mm}$
1.6 sextet 10 mm
2.3 t 10 mm .
ii) $\quad \mathrm{CMR}: \delta 18(\mathrm{Str}), 38(\mathrm{~m}), 214(\mathrm{w})$

PMR: $\delta \quad 1.2 \mathrm{~d} 12 \mathrm{~mm}$
2.8 septet 2 mm .
b) Deduce the structure from the spectral data given below

MF : $\mathrm{C}_{7} \mathrm{H}_{14} \mathrm{O}_{2}$
Mass : $\frac{m}{e} 130,115,98,73,43$.
CMR : $\delta 208(\mathrm{~s}), 75(\mathrm{~s}), 54(\mathrm{t}), 50(\mathrm{q}), 33(\mathrm{q}), 25(\mathrm{q} . \mathrm{str})$.
c) Arrange the following underlined protons in increasing order of chemical shift. Justify.

d) Compound $\underline{D}$ is converted into $\underline{E}$ and then to stereoisomers $\underline{F}$ and $\underline{G}$ as shown in the reaction given below. How will you follow the reaction sequence by PMR spectroscopy? How will you distinguish between stereoisomers $\underline{\mathrm{F}}$ and $\underline{\mathrm{G}}$ by the same method?

e) Use the ${ }^{13} \mathrm{C}$ chemical shifts listed below to choose between the following isomeric structural possibilities : $\delta c$ (number of attached protons) 170.0 (0), 168.9 (0), 165.6 (0), 150.4 (0), 133.3 (1), 131.4 (1), 124.1 (1), 123.5 (1), 20.8 (3).


(B)


(D)

Q3) Discuss any three of the following :
a) NOE using Solomon's diagram.
b) Factors affecting vicinal coupling constants.
c) Fragmentation patterns of carbonyl compounds in mass spectrometry.
d) Factors affecting signal intensities in NMR.

## SECTION - II

Q4) Answer any three of the following :
a) Give a brief account of analysers used in mass spectrometry.
b) The mass spectra of a compound shows the following ions. Find a structure consistent with the data.
$\frac{m}{e}: 114$ (34), 113 (7), 112 (100), 78 (40), 79 (49), 51 (14), 56 (12), 39 (8).
c) The M.S. of 1-phenyl, 2-phenyl, 3-phenyl pentanes and 2-phenyl - 2 methylbutane are shown below. Assign each structure to a letter giving reason.

A: $\frac{m}{e}: 133$ (str.), 106, 105
B : $\frac{m}{e}: 133$ (weak), 120, 119.
$\mathrm{C}: \frac{m}{e}: 133$ (str.), 120, 119.
$\mathrm{C}: \frac{m}{e}: 92,91$.
d) Give genesis of important ions in the following :
i) $\square \mathrm{NHEL}$

$$
\frac{m}{e}: 85,84,70,56 .
$$

ii)


$$
\frac{m}{e}: 123,93,77,65,51 .
$$

Q5) a) Assign the signals to the various protons of compound $\underline{X}$. How the signals indicate the stereochemistry shown by $\underline{X}$ ?

$\delta \mathrm{H}: 1.21(3 \mathrm{H}, \mathrm{d}, \mathrm{J}=7 \mathrm{~Hz}), 1.29(3 \mathrm{H}, \mathrm{t}, \mathrm{J}=9 \mathrm{~Hz}), 1.60(1 \mathrm{H}, \mathrm{t}, \mathrm{J}=6 \mathrm{~Hz})$,
$1.77(1 \mathrm{H}$, dd $\mathrm{J}=6,13,7 \mathrm{~Hz}), 2.16(1 \mathrm{H}, \mathrm{dt}, \mathrm{J}=6 \& 13 \mathrm{~Hz})$,
$4.18(2 \mathrm{H}, \mathrm{q}, \mathrm{J}=9 \mathrm{~Hz}), 6.05(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=20 \mathrm{~Hz})$ and $6.62(1 \mathrm{H}, \mathrm{dd}, \mathrm{J}=13,20 \mathrm{~Hz})$.
b) A compound with MF $\mathrm{C}_{10} \mathrm{H}_{12} \mathrm{O}_{2}$ shows the following spectral data. Interpret the data and arrive at a reasonable structure. Justify your answer.

MR : $\delta: \quad 146.4(\mathrm{~W}), 143.9(\mathrm{~W}), 137.8,131.9(\mathrm{~W}), 121.2,115.5,114.2$, 111.1, 55.8, 39.9.

MR : $\delta: \quad 3.32(\mathrm{bd} \mathrm{J}=6.7 \mathrm{~Hz}, 2 \mathrm{H}), 3.87(\mathrm{~S}, 3 \mathrm{H}), 4.52(\mathrm{bs}, 1 \mathrm{H}, \mathrm{exch})$, 5.03 (ddt, $\mathrm{J}=17,2,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.15(\mathrm{ddt}, \mathrm{J}=9.7,2,1.5$ $\mathrm{Hz}, 1 \mathrm{H}), 5.95(\mathrm{ddt}, \mathrm{J}=17,9,767,1 \mathrm{H}), 6.61(\mathrm{dd} \mathrm{J}=8.4$, $2 \mathrm{~Hz}, 1 \mathrm{H}), 6.68(\mathrm{~d}, \mathrm{~J}=2 \mathrm{~Hz}, 1 \mathrm{H}), 6.85(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H})$

NOE Irradiate Show NOE

$$
\begin{equation*}
6.68 \delta \quad \rightarrow \quad 3.32 \delta \& 3.87 \delta \tag{5}
\end{equation*}
$$

c) The CMR spectra of Rapamycin $\underline{X}$ shows following signals. As sign the signals to different carbons. Explain your answer.

cmR:
$195 \cdot 4(s)$
$170.4(s)$
$165.6(s)$
$98.0(s)$
$74.5(d)$
$72.8(d)$
$72.2(t)$
$58.4(q)$
$56.3(q)$.

$$
\begin{aligned}
& 52.4(q) \\
& 51.5(d) \\
& 3.9 .1(t) \\
& 3.4 .2(d) \\
& 3.1 .7(t) \\
& 26.5(t) \\
& 2.4 .4(t) \\
& 2.1 .2(t) \\
& 15.5(q)
\end{aligned}
$$

Q6) You are provided with the spectra of a compound. Analyse these spectra and from your analysis arrive at a structure consistent with the data: Justify the structure.

$\square$
M.Sc.

ORGANIC CHEMISTRY

# CH-352 : Organic Stereochemistry (2008 Pattern) (Semester-III) 

Time: 3 Hours]
[Max. Marks : 80
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 any four of the following:
a) Cyclohexene on treatment with performic acid followed by hydrolysis gives trans-1, 2-diol, where as trans-cyclodecene on similar reaction gives trans-1, 6-diol.
b) Chair-chair form of bicyclo [3,3,1] nonane is less stable than boat-chair form, while cyclohexene-1, 3-dicarboxylic acid anhydride exists in chair-chair. Explain.
c) Which of these two compounds would form an epoxide on treatment with base? Explain your answer.


I

d) Explain the following observations.

$\mathrm{n}=7$ $\qquad$ only cis olefin
$\mathrm{n}=8$ $\qquad$ only cis olefin
$\mathrm{n}=9$ $\qquad$ only trans olefin
e) Draw the stereostructures of all distereomers of perhydroanthracene. Explain their order of stability.

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


$$
\xrightarrow{\mathrm{Et} \stackrel{\ominus}{\mathrm{O}} \stackrel{\oplus}{\mathrm{Na}}}
$$

b)


$$
\xrightarrow[\Delta]{\mathrm{ACOH}} \rightarrow 9+9
$$

c)

d)

e)


Q3) Write short notes on any three of the following:
a) Concept of I-strain.
b) Stereochemical restrictions of Bredt's rule.
c) 3-Alkyl ketone rule.
d) Chromatographic techniques in resolution.

## SECTION-II

Q4) Answer the following questions (any three):
a) Deduce the relative configuration at $\mathrm{C}_{5}$ and $\mathrm{C}_{6}$ in dihydro codeine.
b) Prove that four alkoids i.e. quinine, quinidine demethoxy quinidine and cinchonidine have identical configuration at $\mathrm{C}_{3}$ and $\mathrm{C}_{4}$ carbon.
c) How will you prove that cinchonine and cinchonidine have different configuration at $\mathrm{C}_{8}$ and $\mathrm{C}_{9}$ chiral centres.
d) Give the structure at enhydrin and show all the chiral centres.

Q5) Attempt any four of the following:
a) Write short account of 'chiral auxillaries' with suitable examples.
b) Give the conventions to represent organic molecules.
c) Which of the following compounds are optically active? Why?



d) Write Pro-R and Pro-S configurations for the underlined H -atoms.

e) Explain the difference between the Cram and Felkin rule. Give the products obtained in the following reaction.


Q6) a) Predict the product is in the following reactions. Justify your answer with the help of stereochemistry and mechanism. (Any three)

b) Solve the following (Any one)
i) Suggest the reagent and stereochemistry of the following reaction.




ii) Write short note on Sharpless asymmetric epoxidation.
c) Complete the following reaction sequence. Rewrite the intermediates. Explain your answer.


## ORGANIC CHEMISTRY

## CH-353 : Free Radicals, Photochemistry and Pericyclic Reactions (2008 Pattern) (New) (Semester-III)

Time : 3 Hours]
[Max. Marks : 80
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) Suggest suitable mechanism for any four of the following:
a)

b)

c)

d)

e)


Q2) a) Explain decomposition of diazo-compounds with suitable examples.[4]
b) Predict the product/s indicating mechanism in any five of the following:
i) $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{C} \cdot \mathrm{HgCl}+\mathrm{H}-\mathrm{C} \equiv \mathrm{C} \cdot \mathrm{CO}_{2}$ me $\xrightarrow{\mathrm{NaBH} 4} \&+$
ii)

iii)

iv) 4,5-dimethyl-2-hexanone $\xrightarrow{h \nu} A+B+C$
v)

vi)


Q3) a) Explain any two of the following:
i) Aromatic amines on sandmeyer reaction in a solution containing styrene using cuprous chloride give appreciable quantity of chloro-arylation product.
ii) In the photochemical dimerisation of g-carbethoxy-anthracene


Only 'head to head' dimer is formed but no 'head to tail' dimer.
iii) Ortho substituents are generally more effective than para-substituents in promoting dissiociation of hexa-arylethanes at room temperature.
b) Write short notes on any two of the following:
i) Autoxidation
ii) Barton reaction
iii) Jablonski Diagram

## SECTION-II

Q4) a) Using the aromatic Transition state concept predict whether $\pi^{2 s}+\pi^{2 s}$ and $\pi^{4 s}+\pi^{2 s}$ cyclo additions are thermally or photochemically allowed.
b) Predict the product/s any four of the following reactions. Explain their stereochemistry and mechanism.
[8]

ij)





Q5) a) Explain with the help of FMO approach whether autorafacial [ 1,7$]$ shift of hydrogen is thermally or photochemically allowed.
b) Explain the mechanism for any four of the following:


jj)


iii)


v)




Q6) a) Complete any two of the following
Synthetic sequences indicating all intermediates and reagents required.



b) Discuss in detail the retrosynthetic analysis of Isocomene.

## $\rightarrow \rightarrow \rightarrow$

## CH-390 : Electro Analytical and Current Analytical Methods in

 Industries(2008 Pattern) (Semester - III)

## Time : 3 Hours]

[Max. Marks: 80

## Instructions to the candidates:

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

## SECTION - I

Q1) Attempt any four of the following :
a) Write a note on anodic stripping voltametry.
b) Explain the factors affecting polarographic wave.
c) Describe the construction and working of DME. Give its advantages.
d) A peak current of $22.5 \mu \mathrm{~A}$ was observed at a scan rate of $0.270 \mathrm{~V} / \mathrm{s}$ at a disc electrode during the forward scan of triangular wave voltammogram. Calculate the peak current at a scan rate of $50.0 \mathrm{mV} / \mathrm{S}$ assuming a reversible electrochemical reaction.
e) The Polarogram of 1.25 mM solution of zinc (II) had a average diffusion current of $7.12 \mu \mathrm{~A}$. The capillary characteristic were $\mathrm{t}=3.47$ second $\mathrm{M}=1.42 \mathrm{mg} / \mathrm{s}$. Determine the difussion coefficient of Zinc (II) in solution.

Q2) Attempt any four of the following:
a) Explain the criteria for reversibility of an electrochemical reaction.
b) Write a note on chronoamperometry.
c) Explain an electrochemical deposition method used for synthesis of nano materials.
d) Give a brief account of rotating ring disc electrode.
e) A 25 ml aqueous sample of Fe (II) was assayed in 0.20 M ceriom (II) solution by controlled potential coulometry. At the end point area under current time curve was 20.0 mA min. Determine the concentration of $\mathrm{Fe}(\mathrm{II})$ in sample. The overall reaction was $\mathrm{Ce}^{4+}+\mathrm{Fe}^{2+} \rightarrow \mathrm{Ce}^{3+}+\mathrm{Fe}^{3+}$.

## SECTION - II

Q3) Attempt any four of the following :
a) Discuss the principle of thermometric titrations. Explain the nature of thermometric titration curve for exothermic and endothermic reaction.
b) State and explain the principle of neutron activation analysis. Hence discuss the theory behind it.
c) Discuss the technique double isotope dilution. Give its application.
d) One litre mixture of halides was analysed for its iodide content. 2 ml of labelled iodine having an activity of 5000 counts per 2 minutes were added to it. After through mixing 3 ml of pure iodine were separated and found to give an activity of 6000 counts per 10 minutes. If the background count is 100 for 20 minutes, calculate the percentage of iodide in given mixture.
e) Calculate the percentage of $\mathrm{CaCO}_{3} \& \mathrm{MgCO}_{3}$ in 75 Mg of limestone sample that exhibit thermogram showing weight of 65 Mg at $500^{\circ} \mathrm{C}$ and 50 Mg at $900^{\circ} \mathrm{C}$.
(Given : At wt. $\mathrm{Ca}=40.08, \mathrm{Mg}=24.31, \mathrm{C}=12, \mathrm{O}=16$ ).

Q4) Answer any four of the following:
a) Discuss the difference between DTA and DSC.
b) Explain the technique Nephelometry. Give its applications.
c) Write a short note on electrochemical sensors.
d) Discuss the applications and limitations of radio-reagent methods of analysis.
e) 5 Mg of manganese dioxide powder was irridiated in neutron flux of $10^{7}$ Neutrons per $\mathrm{cm}^{2}$ per sec. for a period of 15 min . Calculate the activity induced in the sample due to manganese dioxide at the end of irradiation after the cooling period of half an hour.

Given for $\mathrm{Mn} \rightarrow t_{1 / 2}=2.58 \mathrm{hr} ; \sigma=13.3$ barn
$\%$ abundance of $\mathrm{Mn}=100$; At. wt of $\mathrm{Mn}=54.93$

$$
\mathrm{O}=16
$$

## $t+t+$

$\square$

# CH-391 : Environmental and Analysis of Industrial Materials (2008 Pattern) (Semester - III) 

## Time : 3 Hours]

[Max. Marks: 80

## Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory and carry equal marks.
3) Neat diagram must be drawn wherever necessary.
4) Use of logarithmic table, non-programmable calculators are allowed.

## SECTION - I

Q1) Attempt any four of the following :
a) Discuss any one method for determination of phosphorus from fertilizers.
b) Explain the analytical method for estimation of sodium from glass.
c) Explain the term propellant and explosive. Describe analytical method for determination of calcium in propellant.
d) Give the procedure for determination of alcohol soluble material from soap.
e) Find the amount of K present in fertilizer sample, in the form of $\mathrm{K}_{2} \mathrm{O}$ if it's elementary K content is $5.4 \%$.
[At. Wts. : K = 39.10, O = 16]

Q2) Attempt any four of the following:
a) Define the terms :
i) Pigment.
ii) Binder.
iii) Vehicle.
iv) Varnish.
v) Flash point.
b) Give the analytical procedure for analysis of any two of the following from hair tonic preparations.
i) $\mathrm{KBrO}_{3}$
ii) Resorcinol.
iii) Salicyclic acid.
c) Write note on :
i) Heat of explosion.
ii) Hygroscopicity.
d) A sample of detergent weighing 0.850 gm was dissolved in water and solution was diluted to 100 ml in volumetric flask, 10 ml of an aliquot of this solution required 12 ml of 0.005 N CETAB solution for complete reaction. Calculate percentage of combined $\mathrm{SO}_{3}$, present in sample.
[At. Wt. $\mathrm{O}=16, \mathrm{~S}=32$ ]
e) A sample of brass weighing 0.40 gm dissolved in mixture of $\mathrm{HNO}_{3}$ and $\mathrm{H}_{2} \mathrm{SO}_{4}$. A 250 ml stock solution was prepared, 50 ml aliquot was taken for determination of Zn as $\mathrm{Zn}_{2} \mathrm{P}_{2} \mathrm{O}_{7}$ gravimetrically. The weight of ppt. was 0.180 gm . Calculate percentage of Zn in brass.
[Given : At. Wts. $\mathrm{Zn}=65, \mathrm{P}=30.97, \mathrm{O}=15.99$ ]

## SECTION - II

Q3) Answer any four of the following:
a) Outline analytical procedure for the estimation of Cu from Cupronickel alloy.
b) What is Sludge? Describe the method of sludge disposal.
c) How $\mathrm{SO}_{\mathrm{x}}$ is generated? Give Hazardous effects on materials. How is it controlled?
d) Give the composition of steel. Discuss the analytical method for determination of Chromium from steel.
e) In the determination of COD 100 ml of waste water sample reflux with $10 \mathrm{ml} 0.1 \mathrm{~N} \mathrm{~K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ solution and $20 \mathrm{ml} \mathrm{H}_{2} \mathrm{SO}_{4}$ solution. The solution was titrated with 0.1 N FAS solution. The back titration reading was 17.0 ml . For blank titration, 10 ml of $0.1 \mathrm{~N} \mathrm{~K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ solution required 19 ml of 0.1N FAS solution. Calculate Chemical Oxygen Demand (COD) of waste water sample.

Q4) Attempt any four of the following :
a) Explain the analytical procedure for estimation of My from dolomite Ore.
b) Write note on settling chamber.
c) How does catalytic convertor reduce the air pollution from petrol powered vehicle?
d) Mention the following terms :
i) Aerosol.
ii) BOD.
iii) COD.
iv) Mist.
v) Dust.
e) 0.210 gm of cupronickel alloy was dissolved by acid treatment and the solution was diluted to 100 ml . In gravimetric estimation of Ni as $\mathrm{Ni}-$ DMG. 25 ml diluted solution gave 0.168 gm of Ni -DMG ppt. after removal of Cu . Calculate percentage of Ni in the sample.
[Given : At. Wts. : Ni = 58.6 Ni-DMG = 288.6]

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## Time : 3 Hours]

[Max. Marks: 80
Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory and carry equal marks.
3) Neat diagrams must be drawn wherever necessary.
4) Use of logarithmic tables/non-programmable calculator is allowed.
5) Use of graph paper is allowed.

## SECTION-I

Q1) Attempt any four of the following:
a) State and explain the Ohm's law. Explain with suitable example how this law is useful in circuit analysis.
b) Explain the scope of microprocessor control and computers in analytical laboratories.
c) Explain the term zener diode and describe how it is used for voltage regulation.
d) Draw the circuit diagram showing forward and reverse bias ofp-n junction.
e) Calculate the reactance of $0.07 \mu \mathrm{f}$ capacitor of a frequency 6 kHz and 50 MHz .

Q2) Attempt any four of the following:
a) Explain the properties of ideal amplifier. Draw the circuit diagram and discuss the working of an amplifier as differentiator and integrator.
b) Write short note on centrifugal force analyzer.
c) Draw the circuit symbol of the following:
i) Amplifiers
ii) Transistors
iii) Photodiodes
iv) Light emitting diodes
v) Photo resistors
d) Write the binary equivalent numbers 35 and 42 add these binary numbers and convert the answer into decimal equivalent.
e) Parallel combination of three resistance of value $15 \Omega, 20 \Omega$ and $35 \Omega$ are connected across 70 V battery. Find the total resistance and total current.

## SECTION-II

Q3) Attempt any four of the following:
a) Compare the flame emission and atomic absorption spectroscopic techniques of analysis with respect to principle and method of analysis.
b) Give a brief account of radioimmuno assay with special reference to principle and application.
c) Compare supercritical fluid with gas and liquid. Give comparision between supercritical fluid chromatography with other column chromatography techniques.
d) Explain the type of transition tunable laser. Classify medium pumping and controlling mechanism.
e) A 400 mg sample of hair from a young child is digested in $\mathrm{HNO}_{3}-\mathrm{HClO}_{4}$ and diluted to 25 ml . A 10 ml aliquot is diluted to 25 ml and analysed with a cadmium hollow cathode tube. The absorbance reading is 0.17 . To a second 10 ml aliquot 1 ml of a 0.5 ppm standard. Cadmium solution is added followed by dilution to 25 ml and analyzed for cadmium. The absorbance reading is 0.20 . Calculate the cadmium content in the hair sample and compare it with the mean value of 8.0 ppm found for children.

Q4) Attempt any four of the following:
a) Explain the internal standard method in AAS with suitable example.
b) Define spectrum. Describe in brief the principle and mechanism of emission, fluorescence and absorption spectra.
c) Compare RIA and ELISA technique. Explain their relative merits and demerits.
d) Describe how the laser enhanced ionisation technique is useful for detection of various gases, liquid and solids.
e) A well water sample is analysed by flame photometery for Na at 589.5 nm . The emission scale. A series of standard solution gives the following result.

| Na in ppm | Emission Reading |
| :--- | :--- |
| 0.1 | 0.21 |
| 0.5 | 0.75 |
| 2.5 | 3.3 |

Determine ' Na ' level in ppm in well water sample.

## $7 \rightarrow 7$

M.Sc. - II

## ANALYTICAL CHEMISTRY

# CH-380 : Pharmaceutical Analysis (2008 Pattern) (Semester-III) (Optional) 

## Time : 3 Hours]

[Max. Marks : 80
Instructions to the candidates:

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

## SECTION-I

Q1) Attempt any Four of the following:
a) Explain process errors and packing errors.
b) Write a note on "Prediction of shelf life of pharmaceutical products".
c) What is limit test? Explain the limit test for lead.
d) Give any one method for biological assay of insuline.
e) 1.12 g of salicylic acid $\left[\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{O}_{3}\right]$ sample was dissolved in 15 ml ethanol. To this 50 ml of 0.5 M sodium hydroxide $\mathrm{Sol}^{\mathrm{n}}$ was added and it is boiled for 15 minutes on cooling excess of alkali was titrated with 0.5 M hydrochloric acid using phenol red indicator. The titre reading was 25.0 ml . The blank titration reading was 49.8 ml . Determine the amount of salicylic acid in the sample.

Q2) Answer any Four of the following:
a) Give a brief account of sources of impurities in pharmaceutical preparations.
b) What are aerosois? How are they prepared? Give its advantages and disadvantages.
c) Explain the analytical procedure for determination of moisture from pharmaceutical product using K.F. method.
d) How sulphated ash from vegetable drug is determined?
e) 0.28 g oxyphenbutazone $\left[\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{3} \cdot \mathrm{H}_{2} \mathrm{O}\right]$ sample was dissolved in 25 ml acetone \& solution was titrated with 0.1 N sodium hydroxide using bromothymol blue indicator. The titration reading was 7.5 ml . Calculate the percentage of oxyphenbutazone in the sample.

## SECTION-II

Q3) Answer any Four of the following:
a) Describe dry heat sterlization in detail. Give the advantages and disadvantages of it.
b) What are the tablets? Give assay of aspirin from APC tablet.
c) Differentiate between injection and infasion.
d) Define ointment. Explain various types of ointment bases.
e) 0.32 g of sulphadizine $\left[\mathrm{C}_{10} \mathrm{H}_{10} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{~S}\right]$ was dissolved in 10.0 ml concentrated hydrochloric acid and 50 ml of water. After cooling this solution to $15^{\circ} \mathrm{C}$, it was titrated with $0.1 \mathrm{~N} \mathrm{NaNO}_{2}$ using acriflarin indicator. The burette reading was 10.1 ml . Calculate the percentage of sulphadiazine in the given sample.[Given. At. Wt. $\mathrm{C}=12, \mathrm{H}=1, \mathrm{~N}=14, \mathrm{O}=16$ and $\mathrm{S}=32$ ]

Q4) Attempt any four of the following:
a) Write a note on role of FDA.
b) Give a brief account of different dosage forms.
c) Explain the major steps involved in the development of new drug.
d) Describe the terms Gels and Lotions.
e) Explain the procedure for determination of proteolytic activity.

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M.Sc. - II

## ANALYTICALCHEMISTRY

CH-381 : Medicinal Chemistry (2008 Pattern) (Semester-III) (Optional)

## Time : 3 Hours]

[Max. Marks: 80
Instructions to the candidates:

1) Answers to the two sections should be written in separate answer books.
2) All questions are compulsory and carry equal marks.
3) Neat diagrams must be drawn wherever necessary.

## SECTION-I

Q1) Answer any Four of the following:
a) Give an account of chemical assay of drugs.
b) Discuss the relationship between free - Wilson and Hansch analysis.
c) What is drug? Classify the drugs on the basis of therapeutic action.
d) Explain the phenomena of concept of pro-drug and soft drug in detail.
e) Discuss concept of drug receptors and drug receptor interactions.

Q2) Attempt any Four of the following:
a) Discuss occupancy theory and induced fit theory.
b) Explain the use of pharmacokinetics in drug development process.
c) Define and explain : $\mathrm{LD}_{50}$, Drug absorption, Drug elimination and $\mathrm{ED}_{50}$.
d) Write a note on 'molecular modelling'.
e) Discuss the concept of chiral drug with suitable examples.

## SECTION-II

Q3) Attempt any Four of the following:
a) What are sedatives and hypnotics? Give their classification.
b) Discuss the mode of action of sulphonamides and cipro-floxacin.
c) Explain the use of harmones and natural products as antineo plastic agents.
d) Write a brief account of benzodiazapines.
e) Give the synthesis of
i) Sorbitrate
ii) Streptomycin

Q4) Attempt any four of the following:
a) Give the structure and detail mode of action of chloramphenicol.
b) Explain the CNS depressants drug with suitable examples.
c) Define and explain the terms:
i) Sedatives
ii) Antidepressants
d) Discuss the neurochemistry of mental diseases.
e) Discuss the synthesis of any one cardio vascular drug.

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## PHYSICALCHEMISTRY

## CH-410 : Molecular Structure and Spectroscopy (2008 Pattern) (Semester - IV) (Old)

## Time : 3 Hours]

[Max. Marks: 80
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 indicates full marks.
4) Use of logarithmic tables/calculator is allowed.
5) Neat diagrams must be drawn wherever necessary.

## Physico-Chemical Constants

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

## SECTION - I

Q1) Attempt any three of the following:
a) State the essential characteristics of the instrumentation for high resolution NMR.
b) Discuss the factors influencing the coupling constant in NMR spectra.
c) With explanation, draw a schematic of high resolution NMR spectra of $\mathrm{HPF}_{2}$ with respect to nuclei of ${ }^{1} \mathrm{H},{ }^{31} \mathrm{P}$ and ${ }^{19} \mathrm{~F}$.
d) Write a note on : FT NMR spectroscopy.
e) Explain the concept of 'electric field gradient' and quadrapole coupling constant.

Q2) Attempt any three of the following:
a) Describe the working of magic T in the instrument of ESR.
b) What is $g$-value? Discuss the factors affecting the $g$-value.
c) Explain the terms - Kramers degeneracy, zero field splitting and hyperfine coupling constant in ESR studies.
d) Explain the principle of ESR. Why does the source have to be from the microwave region for observing ESR?
e) With the help of a schematic diagram, explain the working of PAS.

Q3) Solve any two of the following :
a) Calculate the frequency separation of nuclear spin states in ${ }^{13} \mathrm{C}$ nucleus with a magnetic field of 14.5 T , the magnetogyric ratio being $6.73 \times 10^{7} \mathrm{~T}^{-1} \mathrm{~S}^{-1}$.
b) The benzene radical anion has $g=2.0025$. At what field should one search for resonance in a spectrometer operating at 9.302 GHz ?
c) Predict the intensity distribution in hyperfine lines of the ESR spectrum by the radicals ${ }^{\circ} \mathrm{CH}_{3}$ and ${ }^{\circ} \mathrm{CD}_{3}$.

## SECTION - II

Q4) Attempt any three of the following:
a) State the phase problem of XRD and outline the techniques used to overcome it.
b) Give a brief account of Bragg's method used in the elucidation of crystal structure. What are the limitations of Bragg's method?
c) Define and explain the terms 'scattering factor' and 'Structure factor' used in XRD.
d) Describe the experimental arrangement for the study of electron diffraction of gases.
e) State and explain the XRD and interference of wave motions.

Q5) Attempt any three of the following :
a) Distinguish between Gouy and Faraday methods.
b) Derive the Wierl equation used in electron diffraction technique.
c) How is the phenomenon of neutron diffraction experimentally studied?
d) Derive the Van-Velck formula for magnetic susceptibility.
e) Discuss the applications of electron diffraction technique.

Q6) Solve any two of the following:
a) Calculate the glancing angle.
[Given : $\mathrm{d}=400 \mathrm{pm}, \lambda=153.9 \mathrm{pm}, \mathrm{n}=1$ ]
b) The mass and density of an atom are 63.5 and $8.94 \mathrm{gcm}^{-3}$ respectively. The atom has FCC structure. Calculate the radius of the atom.
c) Calculate the volume and mass paramagnetic suceptibilities of a sample of a complex salt with three unpaired electrons at 298 K .
[Given : density $=1.85 \mathrm{gcm}^{-3}$, molar mass $=228 \mathrm{gmol}^{-1}$ ]

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## PHYSICALCHEMISTRY

CH-415 : Special Topics in Nuclear Radiation Chemistry (New) (2008 Course) (Semester - IV)

Time : 3 Hours]
[Max. Marks : 80
Instructions to the candidates:

1) Answers to the TWO sections should be written in SEPERATE 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
2) Boltzmann Constant
3). Planck Constant
3) Electronic Charge
4) 1 eV
5) Gas Constant
6) Faraday Constant
7) Speed of light
8) 1 cal
9) Lamu
10) Bohr magneton
11) Nuclearmagneton
12) Mass of an electron
$\mathrm{N}=6.022 \times 1 \mathrm{C}^{23} \mathrm{~mol}^{-1}$
$\mathrm{k}=1.38 \times 10^{-16} \mathrm{erg} \mathrm{K}^{-1}$ molecule ${ }^{-1}$
$=1.38 \times 10^{-23} \mathrm{~J} \mathrm{~K}^{-1}$ molecule ${ }^{-1}$
$\mathrm{h}=6.626 \times 10^{-27} \mathrm{erg} \mathrm{s}$
$=6.626 \times 10^{-34} \mathrm{~J} \mathrm{~s}$
$\mathrm{e}=4.803 \times 10^{-10} \mathrm{esu}$
$=1.602 \times 10^{-19} \mathrm{C}$
$=23.06 \mathrm{k} \mathrm{cal} \mathrm{mol}^{-1}$
$=1.602 \times 10^{-12} \mathrm{erg}$
$=1.602^{-} \times 10^{-19} \mathrm{~J}$
$=8065.5 \mathrm{~cm}^{-1}$
$\mathrm{R}=8.314 \times 10^{7} \mathrm{ergK}^{-1} \mathrm{~mol}^{-1}$
$=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$=1.987 \mathrm{cal} \mathrm{K}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{F}=96487 \mathrm{C}^{\text {equiv }}{ }^{-1}$
c $=2.997 \times 10^{10} \mathrm{~cm} \mathrm{~s}^{-1}$

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=2.997 \times 10^{8} \mathrm{~m} \mathrm{~s}^{-1}
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=4,184 \times 10^{7} \mathrm{erg}
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=4.184 \mathrm{~J}
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$$
=1.673 \times 10^{-27} \mathrm{~kg}
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$\beta_{e}=-9.274 \times 10^{-24} \mathrm{~J} \mathrm{~T}^{-1}$
$\beta_{\mathrm{n}}=5.051 \times 10^{-27} \mathrm{~J} \mathrm{~T}^{-1}$
$\mathrm{m}_{\mathrm{c}}=9.11 \times 10^{-31} \mathrm{~kg}$

## SECTION - I

Q1) Attempt any three of the following.
a) ${ }^{99 \mathrm{~m}} \mathrm{Tc}$ is called as work horse of nuclear medicines. Explain.
b) Give an account of positron emission tomography technique. Which radioisotopes are used in this technique?
c) Write a note on food preservation by ionizing radiations.
d) Describe the method of separation of lithium isotopes.
e) Discuss the principle involved in separation of radio isotopes.

Q2) Attempt any three of the following.
a) Give an account of liquid radiation waste disposal.
b) Which precautions are to be taken while handling high level radioactive waste.
c) Draw and explain primordial nucleosynthesis.
d) What are meteorities? Write the characteristics of stony, iron and stonyiron meteorites.
e) Draw and explain the layered structure of a star after nucleosynthesis.

Q3) Attempt any two of the following.
a) Write the various reactions in C-N cycle.
b) Complete the following reactions.
i) ${ }^{21} \mathrm{Ne}+\square \rightarrow{ }^{24} \mathrm{Mg}+\mathrm{n}$
ii) ${ }^{12} \mathrm{C}+\square \rightarrow{ }^{20} \mathrm{Ne}+{ }^{4} \mathrm{He}$
iii) ${ }^{12} \mathrm{C}+{ }^{12} \mathrm{C} \rightarrow \square+{ }^{1} \mathrm{H}$
iv) ${ }^{71} \mathrm{Ga}+\square \rightarrow{ }^{71} \mathrm{Ge}+\mathrm{e}^{-}$
c) Find the activity of ${ }^{99 m} \mathrm{Tc}$ in technitium generator after 10 h of loading of ${ }^{99} \mathrm{Mo}$.
(Given : intial activity of ${ }^{99} \mathrm{Mo}=20,000 \mathrm{cpm}, \%$ extraction $=90, \mathrm{t}_{1 / 2}$ of ${ }^{99} \mathrm{Mo}=664 \&$ of ${ }^{99 \mathrm{~m}} \mathrm{Tc}=6 \mathrm{~h}$ )

## SECTION - II

Q4) Attempt any four of the following.
a) Describe a typical radiometric titration curve obtained in precipitation reaction where in
i) Substance and reagent both are labelled and
ii) Only substance is labelled
b) Explain the principle and technique of radiometric titration curves based on scattering of $\beta$-particles.
c) Describe with experimental set-up how neutralization reaction can be studied with the help of radioactive kryptonates.
d) Discuss the radiolysis of benzene.
e) Write a note on the radiolysis of alcohol.
f) Discuss the chemical problems in purification and isolation of radioactive species during production in nuclear reactions.

Q5) Answer any four of the following.
a) Give an account of requirements of thin targets and their preparation.
b) Write a note on carriers.
c) Explain molecular kinetics on the basis of Arrhenius law.
d) What is chain reaction? Discuss its basic types.
e) Explain radical scavenging with a suitable example.
f) $12 \mathrm{~cm}^{3}$ of $\mathrm{Zn}^{2+}$ ions labelled with ${ }^{65} \mathrm{Zn}$ were titrated radiometrically with 0.002 M dithiozone. Addition of $1 \mathrm{~cm}^{3}$ of titrant followed by extraction of complex in organic solvent showed a drop in activity from 10,000 counts for 5 minutes to 8000 counts for 5 minutes. Calculate the concentration of $\mathrm{Zn}^{2+}$ in terms of molarity.
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# CH-430 : Inorganic Solids and Heterogeneous Catalysis (2008 Pattern) (Semester - IV) 

## Time : 3 Hours]

[Max. Marks: 80

## Instructions to the candidates:

1) All questions are compulsory.
2) All questions carry equal marks.
3) Neat diagrams should be drawn wherever necessary.

Q1) Attempt any four of the following :
a) Discuss the effect of pH and $\mathrm{SiO}_{2} / \mathrm{Al}_{2} \mathrm{O}_{3}$ ratio on Zeolite synthesis.
b) Discuss Fischer-Tropsch synthesis.
c) What is semi conductor? Discuss the role of semiconductor as a catalyst with suitable example.
d) Describe the methods of preparation of MCM-41? Comment on their acidic properties.
e) Which properties of transition metal makes them good catalyst? Explain.

Q2) Attempt any four of the following:
a) Discuss the role of support in supported metal catalyst.
b) Give an account of chemical reduction method for the synthesis of metal nanoparticles.
c) Which properties of zeolites make them good catalyst? Explain use of zeolite as hydrocracking catalyst.
d) What do you mean by immobilisation? Discuss different methods of immobilization of transition metal complex on a support.
e) Give an account of spectroscopic methods of charecterization for heterogeneous catalyst.

Q3) Answer the following (Any Four) :
a) What do you mean by pillered and intercalated clays? Discuss their use as a catalyst.
b) Write a note on S-N compounds.
c) Define zeolite? Give their classification.
d) Discuss the construction and working of catalytic converter.
e) What is chemical reactor? Discuss the construction, working and application of fixed bed reactor.

Q4) Write a note on (Any Four) :
a) ALPO and SAPO.
b) Silicones.
c) Use of nanoparticles in organic synthesis.
d) Metal clusters.
e) Synthetic methods for bulk metal catalysts.

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## CH - 445 : Inorganic Applications in Industry, Biotechnology and Environmental Chemistry <br> (2008 Pattern) (Semester - IV)

## Time : 3 Hours]

[Max. Marks : 80
Instructions to the candidates:

1) Attempt any two sections from the following.
2) Both sections should be written in the same answer book.
3) All questions are compulsory.
4) Figures to the right indicate full marks.
5) Neat diagrams must be drawn wherever necessary.
6) Use of logrithmic table/calculator is allowed.

## SECTION - I

(Applications of Inorganic Materials)
Q1) Attempt any three of the following:
a) What is meant by term pigment? Explain the following properties of inorganic pigments.
i) Colour and tints,
ii) Reactivity with vehicle
iii) Resistance to light
iv) Pigment size \& shape
b) Give an account of preparation of copper dyes from O-hydroxy diaryl azo compounds and O-halogeno-O-hydroxy diaryl azo compounds.
c) Explain two methods of electroplating of tin.
d) Write a note on Luminous and fluorescent pigments.

Q2) Attempt any three of the following:
a) Explain the methods for electroplating of precious metals.
b) Explain the production and properties of glass fibers for reinforcing plastic resin.
c) Explain the microstructure of soft and hard wood.
d) Gvie in details production of portland cement.

Q3) Write short notes on any two:
a) Alloy plating.
b) Carbon fibre reinforced epoxy resin.
c) Natural earth colour pigment.

## SECTION - II

(Environmental Chemistry)
Q4) Attempt any three of the following:
a) Compare aerobic and anaerobic treatment process.
b) What does primary and secondary treatment in a sewage treatment plant removes from the waste stream?
c) What is powerball? Draw a schematic diagram of plant for producing powerball. How is the hydrogen gas liberated from a powerball? How is the powerball manufactured?
d) Mercury $\left(\mathrm{Hg}^{+2}\right)$ has at $t_{1 / 2}$ of 8 days. If a person injects $3 \mathrm{mg} /$ day. Calculate the steady state concentration of mercury.

Q5) Attempt any three of the following:
a) Define pE . What is the range of pE in natural water? Asample from lake gave a $\mathrm{pE}=10.5$ does the lake favour oxidation?
b) Name the instrumental methods for the determination $\mathrm{Hg}, \mathrm{Cd}, \mathrm{As}, \mathrm{Pb}$. Explain cold-vapour atomic absorption determination of mercury from polluted water.
c) What is meant by point and non-point sources of pollution? Give an example of each.
d) What do you understand by electrodialysis? Explain its use in environmental analysis.

Q6) Write short notes on any two.
a) Reverse osmosis.
b) Energy from biomass.
c) Biorefractory organic pollutant.

## SECTION - II

(Biotechnology)
Q7) Answer any three of the following:
a) Discuss the applications of genetic engineering.
b) With any two examples explain how biotechnology is related to other branches of science \& technology?
c) Give the stages involved in tissue culture.
d) Describe the process of producing food from fungi.

Q8) Attempt any three of the following:
a) Compare between agricultural \& microbial food production.
b) What are enzymes? Give the conditions in which enzyme remain active.
c) State \& explain main stages involved in making cheese.
d) What is sewage? Can sewage treatment be made effective with the use of microbes \& give examples in support of your answer.

Q9) Write short notes on any two:
a) Vaccines.
b) Scaling up process in biotechnological applications.
c) Batch fermenter and continuous fermenter.

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## ORGANIC CHEMISTRY

## CH-450 : Chemistry of Natural Products <br> (2008 Pattern) (Semester - IV)

## Time : 3 Hours]

[Max. Marks: 80

## 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) Outline the steps involved in the following synthetic sequences. Indicate the reagents used and discuss the mechanism \& stereochemistry involved. (Any four)
a)

b)


c)

d)


Q2) Answer the following (Any three):
a) Describe evidences to establish presence of C-9 methyl group of Hardwickiic Acid.
b) Describe the importance of Deuterium exchange reaction in structure determination of Hydroxy-camptothecin.
c) Give the evidence for the presence of $3,4,5$ trimethoxy benzene \& benzene nucleus with side chain in podophyllotoxin.
d) Give evidence to prove the presence of Hardwickiic Acid.


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Q3) a) Place the appropriate missing reagents / intermediates in the following conversion and explain each step.




b) Complete the following synthesis.


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9 . \frac{\mathrm{KOH}}{\mathrm{H}_{2} \mathrm{O}}
$$



SECTION - II
Q4) a) Explain the role of S-Adenosyl methionine in the formation of O-methyl, N -methyl and C-methyl linkages giving one example of each.
b) Suggest biogenetic scheme for any three of the following :

ii) $2 z, 6 E \mathrm{FPP} \longrightarrow$

iii)

iv)



Q5) Answer any two of the following:
i) Squalene monoepoxide $\rightarrow$

ii) Tyrosine $[2-\mathrm{c}] \rightarrow$ (14) Indicate, the position of label in each step.
iii)


Q6) a) The following terpenes Co-occur in plants. Give the biogenesis of them starting from FPP.


B-bisabolenol


B-acoradiene


Cedrene
b) Give the steps involved in the following conversion. Indicate the position of label in each step and role of pyridoxal phosphate.

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# CHO - 452 : Heterocyclic Chemistry, Chiron Approach and Medicinal Chemistry <br> (2008 Pattern) (Semester - IV) 

## Time : 3 Hours]

[Max. Marks: 80
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) a) Explain the following. (any three)
i) Benzofuran is more stable than furan towards acid.
ii) Thiophene is resistant to ring opening than pyrrole.
iii) Indole undergoes electrophilic substitution reaction at 3-position, while benzothiophene is not so region selective.
iv) Quinoline is used as a solvent in decarboxylation reaction.
b) i) Explain the concept of supramolecular chemistry and discuss its applications.
ii) Give the reactions of following reagents with Quinoline.

1) $\mathrm{LAH}, \mathrm{Et}_{2} \mathrm{O}$
2) $\mathrm{KNH}_{2}, \mathrm{NH}_{3}$ (liq.), $-66^{\circ} \mathrm{C}$
3) $30 \%$ Oleum, $90^{\circ} \mathrm{C}$

Q2) a) Predict the products in any five of the following:
i)
 $\xrightarrow[\text { i1) } \mathrm{NH}_{4} \mathrm{Cl}]{\mathrm{Mg}_{1} \mathrm{THF}}$ ?
ii)

iii)

iv)

v)

vi)

b) Write short note on. (any three)
i) Hantzsch pyridine synthesis.
ii) Feist Benary furan synthesis.
iii) Knorr pyrrole synthesis.
iv) Synthesis of 8-hydroxy equinoline.

Q3) a) Complete the reaction sequence. (any three)
i)

ii)

iii)


iv)

b) i) Write reaction sequence of conversion of salysaldehyde to benzofuran.
ii) Suggest the mechanism for any one of the following.
1)

2)




Q4) Answer any three of the following:
a) Give the reaction sequence for the cen vesion of aldotetrose to adopentose using Kiliani Fischer synthesis.
b) Draw ${ }^{1} \mathrm{C}_{4}$ and ${ }^{4} \mathrm{C}_{1}$ conformations of
i) D-mannose
ii) D-Glucose
c) How oxidation with $\mathrm{HNO}_{3}$ can be used to distinguish between D-erythrose and D-threose?
d) "Reaction of $\mathrm{HIO}_{4}$ with $\mathrm{D}-(+)$-Glucose confirms that it is aldohexose". Explain.

Q5) a) Write synthesis of R-Epichlorohydrin from D-mannitol.
b) Predict the product/s in the following reactions. (any four)

ii)

iii)

iv)


v)
D-mannitol

ii) $\mathrm{PbPAC}_{4}$, Bemene ii) $\overrightarrow{\mathrm{CrO}}_{3}$, acetone

Q6) a) Answer the following. (any two)
i) What are the characteristic of an ideal drug?
ii) Explain in brief the pharmacokinetis (ADME) of drug action.
iii) Explain the mechanism of renal excretion of drugs.
b) Explain the concept of atom economy. Calculate the atom economy for the following reaction, and also explain the efficienty of the reaction. [4]

c) Write any two principles of green chemistry.
d) Discuss non-covalent interactions between drug and receptor.

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ANALYTICAL CHEMISTRY

## CH-481 : Bioanalytical and Forensic Science (2008 Pattern) (Semester - IV)

## Time : 3 Hours]

[Max. Marks: 80

## Instructions to the candidates:

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

## SECTION - I

Q1) Attempt any four of the following :
a) Describe the procedure for the estimation of starch from flour.
b) Outline the procedure for estimation of tannin from tea sample.
c) Write a note on "Analysis of food preservatives".
d) Give the procedure for protein content in jam.
e) A 10 ml milk sample requires 2.3 ml of 0.01 M NaOH solution. Calculate percentage of Lactic acid in given sample. (Mol.wt. of Lactic acid $=90$ ).

Q2) Attempt any four of the following :
a) Describe the method for estimation of phosphate.
b) Discuss the chemistry of vitamin-A with respect to structure, estimation and source.
c) Explain the method for estimation of creatinine in urine sample.
d) How is theobromine estimated in Cocoa?
e) Calculate the HMF content of sample of honey. The absorbance in cell of unit path length was 0.1657 .

## SECTION - II

Q3) Attempt any four of the following:
a) Explain the isolation of barbiturates, from biological sample by procedure 'A'.
b) How heroin is isolated from urine sample? Outline procedure for adsorption and elution.
c) Outline type-B procedure for isolation and determination of stimulants.
d) Explain the procedure type-C for isolation and identification of amphetamines.
e) Caffien is estimated from blood sample by using gas chromatography. The result of analysis were as follows
i) Standard caffien sample $=60 \mu \mathrm{~g} / \mathrm{ml}$.
ii) Peak height of caffien sample $=75 \mathrm{~min}$.
iii) Peak height of caffien in reference standard $=85 \mathrm{~min}$.

Calculate concentration of Caffien in given sample.

Q4) Attempt any four of the following:
a) Define the terms :
i) Addict.
ii) Opium.
iii) CoCa derivative.
iv) Narcotic drug.
b) Explain the rules related to building arrangements in non-bonded laboratory.
c) Write a note on "Illicit Traffic".
d) Write a note on offences and penalties in Psychotropic Substances Acts.
e) Explain the provision made in narcotic and Psycotropic drug rules related to manufacture of manufactured drugs.

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## CH-491 : Polymer Technology

 (2008 Pattern) (Semester - IV) (Old Course)
## Time : 3 Hours]

[Max. Marks: 80
Instructions to the candidates:

1) All questions are compulsory and carry equal marks.
2) Answer to the two sections should be written in separate answer books.

## SECTION - I

Q1) Attempt any four of the following:
a) Explain the salient features of solution condensation polymerisation.
b) What is polymer degradation? Explain degradation by high energy radiation.
c) Discuss the kinetics of cationic polymerisation.
d) Give the method of preparation and uses of
i) Polyurethane
ii) Polyvinyl chloride
e) How polymers are classified on their morphological behaviour.

Q2) Attempt any four of the following:
a) Write a note on "Valcanisation and curing".
b) Explain the term antioxidant? What is the role of antioxidant in the stability of polymer? Explain it with a suitable examples.
c) Discuss two types of termination reaction in free radical chain polymerisation.
d) What are inhibitors? Explain in detail.
e）Complete the following reactions
i）

ii）
 $\xrightarrow[\Delta]{\mathrm{H}_{2} \mathrm{O}}$ ？
iii）

iv）

v）


## SECTION－II

Q3）Attempt any four of the following：
a）Give an account of electrical properties of polymeric material．
b）Explain the term：
i）Colour
ii）Transmittance
iii）Gloss
iv）Transparency
v）Haze
c）Explain the role of TGA and DTA in structure determination of polymers．
d）Write a note on calendering．
e）Determien \％elongation of 12.00 cm polystryene sample that increase in length to 12.5 cm subjected to tensile strength．

Q4）Attempt any four of the following：
a）Describe with a neat diagram，the dry spinning process．
b）Describe in detail the cryscopic method for the determination of number average molecular weight of polymers．
c）Describe in detail the blow－moulding．
d）Explain the term compounding．What are the ingredients used in compounding process？Give the role of eah ingredient．
e）Equal masses of polymer molecules with $\mathrm{M}_{1}=20,000$ and $\mathrm{M}_{2}=2,00,000$ are mixed．Calculate $\overline{\mathrm{M}}_{n}$ and $\overline{\mathrm{M}}_{w}$ ．

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