1 SEM PG (CBCS) CHM C 3

2024

(December)

CHEMISTRY

Paper : 103

(Core Course)

(Physical Chemistry–I)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

Answer **Unit–I, Unit–II** *and* **Unit–III** *in* **separate booklets.**

Unit–I

(Marks : 15)

1. Answer ***any three*** questions : 3×3=9

(a) How does the Third Law of Thermodynamics enable the calculation of absolute entropy for a substance, and what challenges arise in this process, particularly at absolute zero ?

(b) What is fugacity, and how does it provide a more accurate representation of the behavior of real gases compared to ideal gas pressure? Discuss the significance of the fugacity coefficient in this context. 1+1+1=3

(c) How the chemical potential (μ) is mathematically expressed, and what factors influence its value for a given substance? Compare the concept of chemical potential with that of partial molar volume. 1+1+1=3

(d) Derive the relationship of the activity coefficient of an ideal gas with temperature and pressure. Additionally, explain the 'solubility method' used for determining activity and activity coefficients. 1½+1½=3

2. Answer ***any three*** questions : 2×3=6

(a) Explain the relationship between chemical potential and Gibbs free energy. How does this relationship inform our understanding of reaction spontaneity?

(b) *"The fugacity of a gas in a mixture is defined as the product of its mole fraction in the mixture and its fugacity in the pure state, evaluated at the total pressure of the mixture."*

Explain this relationship and its significance in thermodynamics.

(c) Under what conditions does the activity coefficient of a gas equal unity? Calculate the activity of a 0.5 molal $ZnCl_2$ solution, given that the mean ionic activity coefficient ($\gamma\pm$) is 0.9.

(d) Discuss the reasons for the differences between the spectroscopic and calorimetric values of entropy for nitrogen monoxide (NO) and carbon monoxide (CO).

(e) Using 3rd law of thermodynamics prove that—

$$\lim_{T\to 0}(\delta V/\delta T)_P = 0$$

Unit–II

(Marks : 15)

3. Answer ***any three*** of the following questions : 2×3=6

   (a) Show that any linear combination of the functions $sin(4x)$ and $cos(4x)$ is an eigenfunction of the operator $\frac{d^2}{dx^2}$.

   (b) Find the probability of finding a particle in a one-dimensional box in the region $0 \le x \le \frac{3L}{4}$ for n=1.

   (c) A particle is enclosed in a cubic box of length $L(0 \le x \le L)$. Find the degeneracy of the energy level, $E = \frac{29h^2}{8mL^2}$.

   (d) Find the expression of the kinetic energy operator in the position representation.

   (e) Prove that the eigenfunctions corresponding to two different eigen-values of a Hermitian operator are orthogonal.

4. Answer ***any three*** of the following questions : 3×3=9

   (a) Prove that the momentum operator $(\widehat{p_x})$ in the position representation is a Hermitian operator.

   (b) Locate the nodes of the harmonic-oscillator wavefunction with $v = 3$.

   (c) What is the Born interpretation? Discuss the implications of the Born interpretation on the acceptability of the wave function. 1+2=3

   (d) Derive the energy expression of a particle on a ring. Also show that the energies are quantized.

   (e) What is penetration depth ? Find the expression of penetration depth for particle moving in 1-dimension facing a finite barrier with infinite width. ½+2½=3

   (f) Show that the Spherical Harmonics $Y_{1,1}(\theta,\varphi)$ and $Y_{1,0}(\theta,\varphi)$ for a two-particle rigid rotator forms an orthonormal set.

Unit–III

(Marks : 30)

5. Answer ***any four*** questions : 2×4=8

(a) What is the gross selection rule and specific selection rule for the rotational spectrum ?

(b) How does a change in rotational quantum number (K) affect the transition energy of a symmetric top molecule ?

(c) The vibrational structure of the absorption spectrum of O_2 becomes continuous at 56876 cm^{-1}. If the upper electronic state dissociates into one ground state atom and one excited atom with excitation energy $15875 cm^{-1}$, estimate the dissociation energy of the ground state O_2 in $kJmol^{-1}$.

(d) What is a v' progression ? Write the expression for the wavenumber of the (0,0) transition.

(e) The rotational and centrifugal distortion constant of HCl molecule are $10.593 cm^{-1}$ and $5.3\times10^{-4} cm^{-1}$ respectively. Find the vibrational frequency and force constant of the molecule.

(f) Schematically show the difference in the spectrum of a rigid and a non-rigid rotator model.

(g) What are Auxochromes ? Give example.

6. Answer ***any two*** questions : 3.5×2=7

(a) Show that the moment of inertia for HCN molecule (m's are the atomic masses and r's are respective bond lengths) is given by—

$$I = \frac{m_H m_C r_{CH}^2 + m_C m_N r_{CN}^2 + m_N m_H (r_{CH} + r_{CN})^2}{m_H + m_C + m_N}$$

Can the two bond lengths (r_{CH} and r_{CN}) be determined from the above expression ?

(b) The total relative population at a rotational energy E_J varies as—

$$Population \propto (2J+1)\, exp\left(\frac{-E_J}{kT}\right)$$

Show — *i)* graphically and *ii)* explain how the relative population varies with the rotational quantum number (J) in a rigid rotator model. Also, find an expression for J when the population is maximum. 2+1.5=3.5

(c) The values of $\bar{\omega}_e$ and x_e in the ground and the excited state of C_2 are given below :

	$\bar{\omega}_e\ (cm^{-1})$	x_e
Ground state	1641.4	7.11×10^{-3}
Excited state	1788.2	9.19×10^{-3}

Find the number of vibrational levels below the dissociation limit and hence the dissociation energy of C_2 in the ground state. 1.5+2=3.5

7. Answer ***any three*** of the following questions : 2×3=6

(a) The oscillation frequency and anharmonicity constant of an alkali halide are $3000\,cm^{-1}$ and 0.0025 respectively. Find the peak positions (in cm^{-1}) of its fundamental absorption and 1st overtone band.

(b) Among the four fundamental vibrations of CO_2, only one of them is Raman active. Why ?

(c) Why scattered radiations from symmetric vibrations of molecules are plane polarized in Raman spectroscopy ?

(d) It is observed that bond stretching frequency of methanol molecule may change with change in experimental temperature while in case of diethyl ether change is negligible. Explain.

(e) Calculate the value of the energy in ergs of the fifth vibrational level of $^1H^{35}Cl$. Given $\upsilon_e = 2988.95\,cm^{-1}$.

(f) Discuss the.classical theory of Raman effect.

8. Answer ***any three*** of the following questions ? 3×3=9

(a) Calculate the values of $\overline{\omega_e}$ (in cm^{-1}) and anharmonicity constant (x_e) for X-Y bond, whose IR absorption spectrum contains a very intense band at 3019 cm^{-1} and two weak bands at 5668 cm^{-1} and 8700 cm^{-1} respectively.

(b) The molecules A_2B and CD_2 have IR bands with PR counter whereas absent for XY_2. A_2B and the XY_2 molecules have common IR and Raman absorptions whereas absent for the molecule CD_2. Determine the structure A_2B, CD_2 and XY_2 with justification.

Contd.

(c) Discuss the effect of rotation on vibrational spectra when axis of rotation is perpendicular to the direction of vibration under the condition of interaction and non-interaction between the two energies.

(d) Using 4358Å lines of mercury as the source of radiation a Raman line is observed at 4447Å. What is the Raman shift ?

(e) Arrange in ascending order of the intensities of the IR band of the following bonds and justify your answer.

(a) $>C=O$ (b) $>C=C<$ (c) $>C=N-$

Total number of printed pages=10

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Contd.

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Total number of printed pages–12

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(December)

CHEMISTRY

Paper : 102

(Core Course)

(Organic Chemistry–I)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

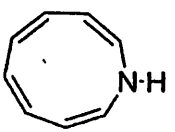
Write the answers of Unit–I, II and V and Unit–III and IV in ***separate books.***

Unit–I

(Marks : 12)

1. Answer ***any six*** of the following questions : 2×6=12

(a) Comment on the aromaticity of the following :

(i) 

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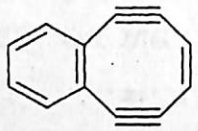
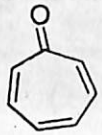
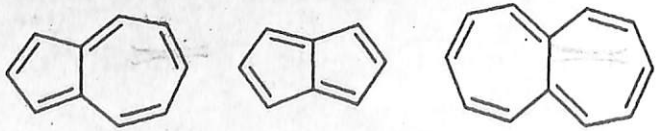
(ii) 

(iii) 

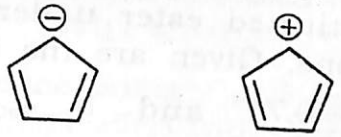
(iv) 

(b) Compound A is stable, polar, and has a dipole moment whereas compound B and C do not have a dipole moment and are relatively unstable. Justify the statement with a proper explanation.



A B C

(c) With the help of the Frost diagram (Frost Circle) validate the aromaticity of compounds A and B.



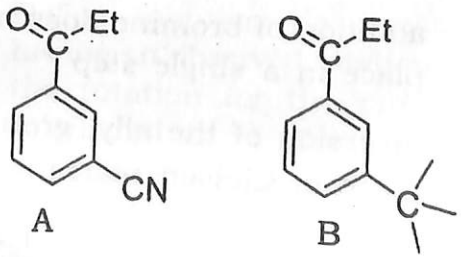
A B

(d) What are crown ethers? Give an example of the utility of crown ethers in organic reactions. 1+1=2

(e) What are catenane and rotaxanes? Give examples. 1+1=2

(f) Write the Hammett equation. Elaborate the physical significance of substituent constant. 1+1=2

(g) Base catalyzed hydrolysis of compound A (with $\sigma_{m\text{-}CN} = 0{\cdot}56$) is faster than the base catalyzed hydrolysis of compound B (with $\sigma_{m\text{-}CH_3} = -0{\cdot}10$). Explain.



A B

Contd.

(h) Base-catalysed hydrolysis of ethyl *m*-nitrobenzoate is 63.5 times as fast as the hydrolysis of the corresponding unsubstituted ester under parallel conditions. Given are the values of $\sigma_{m-NO_2} = 0.71$ and $\sigma_{p-MeO} = -0.27$, calculate the rate for base-catalysed hydrolysis of ethyl *p*-methoxy benzoate under same condition.

Unit–II

(Marks : 12)

2. Answer ***any four*** questions : 3×4=12

(a) Write the kinetic stability and thermodynamic stability products for the addition reaction of *HBr* to 4-methyl-1,3-pentadiene. Draw their energy profile diagram. 1+1+1=3

(b) How will you confirm that :

(i) addition of bromine does not take place in a single step ?

(ii) inversion of the allyl group takes place in Claisen rearrangement ?

1.5+1.5=3

(c) What is anchimeric assistance ? Explain why acetolysis of 4-methoxybutyl brosylate is 650 times faster than that of *n*-butyl brosylate ? 1+2=3

(d) Define primary and secondary kinetic isotope effect with examples. Write the kinetic isotope effect of oxidation of 2-propanol with acidified potassium dichromate. 1+1+1=3

(e) (i) Discuss the mechanism of Claisen rearrangement with the help of crossover experiment. 1.5

(ii) Discuss the mechanism of Cannizzaro reaction with the help of isotopic labeling. 1.5

Unit–III

(Marks : 12)

3. Answer ***any three*** of the following : 3×3=9

(a) Define enantiomeric excess. 2-Butanol having an observed rotation of +9.72 has the rotation for the pure enantiomer calculated as +13.5. 1+2=3

Find out the correct option (Show your calculations) :

(i) Racemic mixture is 72%

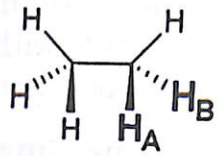
(ii) Racemic mixture is 28%

(iii) Total (-) isomer is 36%

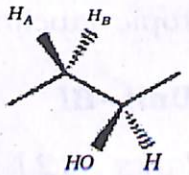
(iv) Total (-) isomer is 14%

(b) Label the pairs of protons shown in boldface in each of the following compounds as homotopic, enantiotopic *or* diastereotopic, as required *(any three)*

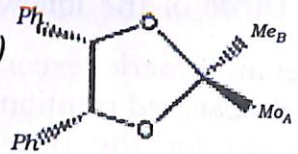
(i)



(ii)

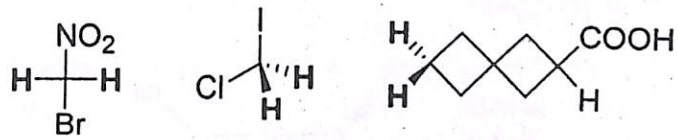


(iii)



(iv)

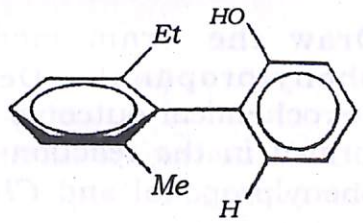
(c) Label the pairs of protons shown in boldface in each of the following compounds as Pro-*R or* Pro-*S*.



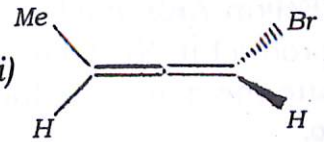
(i) (ii) (iii)

(d) Assign *R or S* for the following compounds ***(any three)***:

(i)



(ii)



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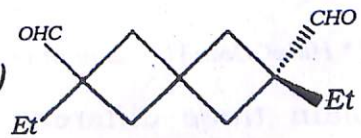
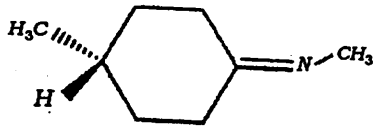
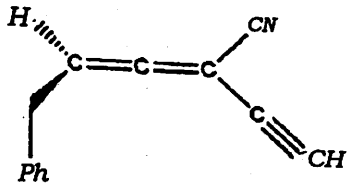


(iv) 

(v) 

4. Answer ***any one*** of the following: 3

(a) Draw the Cram model for (S)-2-phenylpropanal. Determine the sterochemical outcome of the product formed in the reaction between (S)-2-phenylpropanal and CH_3MgI.

(b) Using Felkin-Anh model, identify the major product in the following reaction. Designate the major product as *erythro or threo.*

$$PhC^{*}HMeCOMe\,(R-isomer)+LiAlH_4 \longrightarrow ?$$

(c) Explain *three* different methods of asymmetric induction in a chemical reaction.

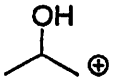
Unit–IV

(Marks : 12)

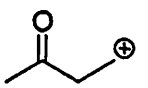
5. Answer *(a)* and ***any two*** of the following: 4+(2×2)=8

(a) Define the terms 'synthon' and 'synthetic equivalents'. Write the synthetic equivalents for the following synthons: 1+3=4

(i)

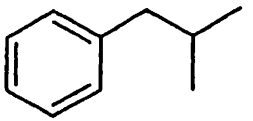


(ii)

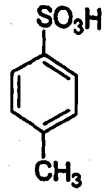


(iii)

(b) Illustrate the importance of Functional Group Interconversion (FGI) in retrosynthetic analysis of the following target molecule to design a logical synthesis.



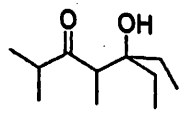
(c) Taking the following example, explain the importance of proper sequence of disconnections to design a proper synthetic strategy.

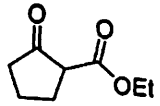


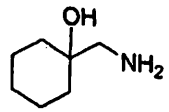
(d) Give a suitable example of a reaction of the type $a^3 + d^2$.

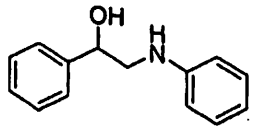
(e) Illustrate with suitable example, the use of aliphatic nitro compound as acyl anion equivalent.

6. Show the retrosynthetic analysis and the corresponding synthesis of each of ***any two*** of the following. (Write the reagents and reaction conditions for the syntheses.) 2×2=4









Unit–V

(Marks : 12)

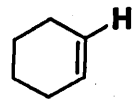
7. Answer ***any six*** of the following: 2×6=12

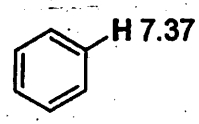
(a) How will you differentiate the following pairs with the help of FTIR? 1+1=2

(i) Maleic acid and fumaric acid

(ii) *o*-hydroxyacetophenone and *p*-hydroxyacetophenone

(b) Explain the chemical shift data of the following protons with proper reason: 1+1=2





(c) How does radio frequency affect NMR? How does radio frequency change with gyromagnetic ratio? 1+1=2

(d) What is NOE in NMR spectroscopy?

(e) Explain the ^1H NMR signals of methylamine and its hydrochloride salt.

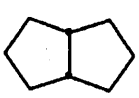
(f) The amount of sample required for recording ^{13}C NMR is more in comparison to the amount required for ^{1}H NMR. Explain.

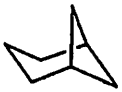
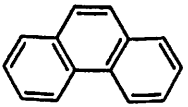
(g) Fill in the blanks :

(i) The number of ^{1}H NMR peaks for vinyl chloride and Methyl-cyclopropane are respectively _____. 1

(ii) Arrange the increasing order of coupling constant values for *gem, cis and trans alkene* _____. 1

(h) Write the number of decoupled ^{13}C NMR peaks for the following :



Total number of printed pages–12

1 SEM PG (CBCS) CHM C 2

2024

(December)

CHEMISTRY

Paper : 102

(Core Course)

(Organic Chemistry–I)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

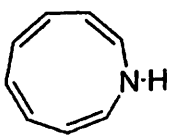
Write the answers of Unit–I, II and V and Unit–III and IV in ***separate books.***

Unit–I

(Marks : 12)

1. Answer ***any six*** of the following questions : 2×6=12

(a) Comment on the aromaticity of the following :

(i) 

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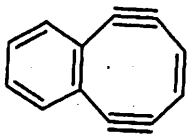
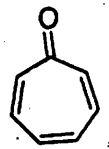
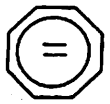
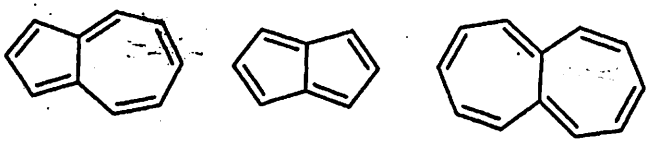
(ii) 

(iii) 

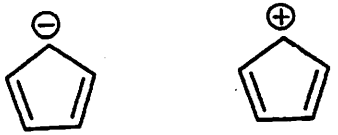
(iv) 

(b) Compound A is stable, polar, and has a dipole moment whereas compound B and C do not have a dipole moment and are relatively unstable. Justify the statement with a proper explanation.



A B C

(c) With the help of the Frost diagram (Frost Circle) validate the aromaticity of compounds A and B.



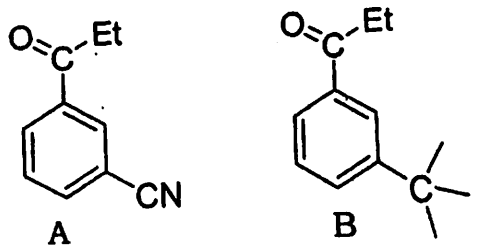
A B

(d) What are crown ethers? Give an example of the utility of crown ethers in organic reactions. 1+1=2

(e) What are catenane and rotaxanes? Give examples. 1+1=2

(f) Write the Hammett equation. Elaborate the physical significance of substituent constant. 1+1=2

(g) Base catalyzed hydrolysis of compound A (with $\sigma_{m\text{-}CN} = 0{\cdot}56$) is faster than the base catalyzed hydrolysis of compound B (with $\sigma_{m\text{-}CH_3} = -0{\cdot}10$). Explain.



A B

(h) Base-catalysed hydrolysis of ethyl *m*-nitrobenzoate is 63.5 times as fast as the hydrolysis of the corresponding unsubstituted ester under parallel conditions. Given are the values of $\sigma_{m-NO_2} = 0.71$ and $\sigma_{p-MeO} = -0.27$, calculate the rate for base-catalysed hydrolysis of ethyl *p*-methoxy benzoate under same condition.

Unit–II

(Marks : 12)

2. Answer ***any four*** questions : 3×4=12

(a) Write the kinetic stability and thermodynamic stability products for the addition reaction of *HBr* to 4-methyl-1,3-pentadiene. Draw their energy profile diagram. 1+1+1=3

(b) How will you confirm that :

(i) addition of bromine does not take place in a single step ?

(ii) inversion of the allyl group takes place in Claisen rearrangement ?

1.5+1.5=3

(c) What is anchimeric assistance ? Explain why acetolysis of 4-methoxybutyl brosylate is 650 times faster than that of *n*-butyl brosylate ? 1+2=3

(d) Define primary and secondary kinetic isotope effect with examples. Write the kinetic isotope effect of oxidation of 2-propanol with acidified potassium dichromate. 1+1+1=3

(e) (i) Discuss the mechanism of Claisen rearrangement with the help of crossover experiment. 1.5

(ii) Discuss the mechanism of Cannizzaro reaction with the help of isotopic labeling. 1.5

Unit–III

(Marks : 12)

3. Answer ***any three*** of the following : 3×3=9

(a) Define enantiomeric excess. 2-Butanol having an observed rotation of +9.72 has the rotation for the pure enantiomer calculated as +13.5. 1+2=3

Find out the correct option (Show your calculations) :

(i) Racemic mixture is 72%

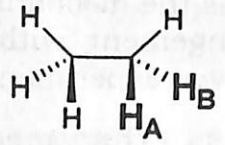
(ii) Racemic mixture is 28%

(iii) Total (-) isomer is 36%

(iv) Total (-) isomer is 14%

(b) Label the pairs of protons shown in boldface in each of the following compounds as homotopic, enantiotopic *or* diastereotopic, as required *(any three)*

(i)



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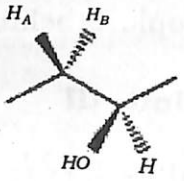

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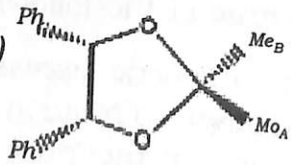

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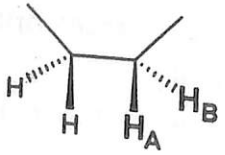
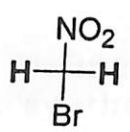
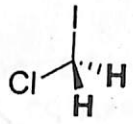


(c) Label the pairs of protons shown in boldface in each of the following compounds as Pro-*R* *or* Pro-*S*.



(i)



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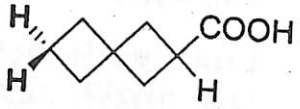
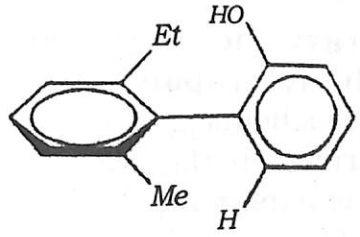


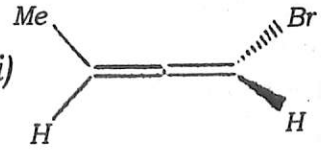
(iii)

(d) Assign *R* *or* *S* for the following compounds ***(any three)***:

(i)



(ii)



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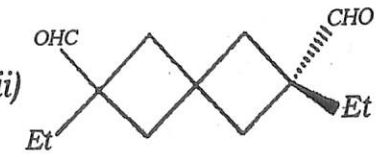
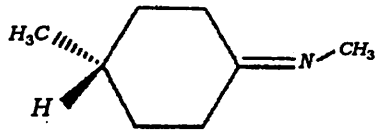
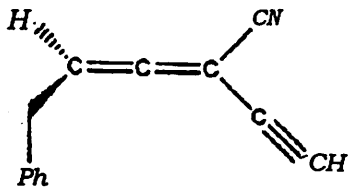


(iv) 

(v) 

4. Answer ***any one*** of the following : 3

(a) Draw the Cram model for (S)-2-phenylpropanal. Determine the sterochemical outcome of the product formed in the reaction between (S)-2-phenylpropanal and CH_3MgI.

(b) Using Felkin-Anh model, identify the major product in the following reaction. Designate the major product as *erythro or threo.*

$$PhC^{*}HMeCOMe\,(R-isomer)+LiAlH_4 \longrightarrow ?$$

(c) Explain *three* different methods of asymmetric induction in a chemical reaction.

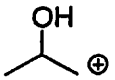
Unit–IV

(Marks : 12)

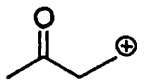
5. Answer *(a)* and ***any two*** of the following : 4+(2×2)=8

(a) Define the terms 'synthon' and 'synthetic equivalents'. Write the synthetic equivalents for the following synthons : 1+3=4

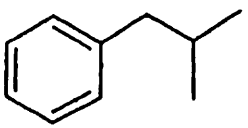

(i)



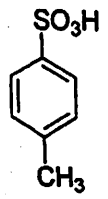
(ii)


(iii)

(b) Illustrate the importance of Functional Group Interconversion (FGI) in retrosynthetic analysis of the following target molecule to design a logical synthesis.



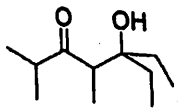
(c) Taking the following example, explain the importance of proper sequence of disconnections to design a proper synthetic strategy.

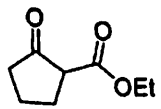


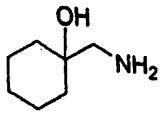
(d) Give a suitable example of a reaction of the type $a^3 + d^2$.

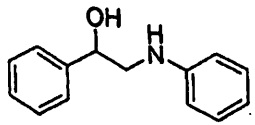
(e) Illustrate with suitable example, the use of aliphatic nitro compound as acyl anion equivalent.

6. Show the retrosynthetic analysis and the corresponding synthesis of each of ***any two*** of the following. (Write the reagents and reaction conditions for the syntheses.) 2×2=4









Unit–V

(Marks : 12)

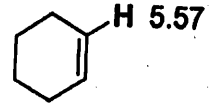
7. Answer ***any six*** of the following : 2×6=12

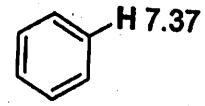
(a) How will you differentiate the following pairs with the help of FTIR ? 1+1=2

(i) Maleic acid and fumaric acid

(ii) *o*-hydroxyacetophenone and *p*-hydroxyacetophenone

(b) Explain the chemical shift data of the following protons with proper reason : 1+1=2





(c) How does radio frequency affect NMR ? How does radio frequency change with gyromagnetic ratio ? 1+1=2

(d) What is NOE in NMR spectroscopy ?

(e) Explain the ^1H NMR signals of methylamine and its hydrochloride salt.

(f) The amount of sample required for recording ^{13}C NMR is more in comparison to the amount required for ^{1}H NMR. Explain.

(g) Fill in the blanks :

(i) The number of ^{1}H NMR peaks for vinyl chloride and Methyl-cyclopropane are respectively _____. 1

(ii) Arrange the increasing order of coupling constant values for *gem, cis and trans alkene* _____. 1

(h) Write the number of decoupled ^{13}C NMR peaks for the following :

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3 SEM PG (CBCS) CHM C 1

2024

(December)

CHEMISTRY

Paper : 301

(Core Course)

(Inorganic Chemistry–III)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

UNIT–I

(Marks : 08)

1. Answer ***any four*** of the following questions : 2×4=8

   (a) Why is there often a discrepancy between the theoretical (calculated) magnetic moment and the experimental magnetic moment of Eu^{3+} ions ?

(b) With the help of a suitable example describe the mechanism by which lanthanide shift reagents (LSRs) induce shifts in the NMR spectra of organic molecules.

(c) Why do actinides exhibit a greater range of oxidation states than lanthanides, and how does this influence their chemical behavior ?

(d) What is elution time in chromatography ? Compare the elution times of La^{3+} and Lu^{3+} ions and discuss the factors contributing to any differences observed. 0.5+1.5=2

(e) Why the lanthanide contraction occurs ? How does it affect the properties of 4d and 5d series transition metals ? 1+1=2

(f) Compare the spectral properties of lanthanides and actinides.

UNIT–II

(Marks : 16)

2. Answer the following questions :

(a) What is Effective Atomic Number (EAN) rule for coordination compound ? Mention if the following compounds obey 18-electron rule or not ? Give reason. 1+3=4

(i) $\left[Ir(CO)Cl(PPh_3)_2\right]$;

(ii) $\left[IrBr_2(CH_3)(CO)(PPh_3)\right]$

Or

Write bnief notes on : 2+2=4

(i) Irving-William order of stability of metal complexes and its significance.

(ii) Relation between stepwise and overall stability constant.

(b) Answer *any three* questions of the following : 2×3=6

(i) What are the conditions for two fragments to be isolobal ? How do you account the isolobality of $Mn(CO)_5$ with CH_3 and Cl.

Contd.

(ii) Discuss the reactivity of carbonyl ligand with reference to various chemical reactions.

(iii) Discuss how the following factors affect the magnitude of C–O stretching frequencies (ν_{CO} cm^{-1}) in various metal carbonyls. 1+1=2

(a) Charge on metal center

(b) Presence of other ligands.

(iv) What are fluxional molecules. Give examples.

(v) With suitable example define oxidative addition and reductive elimination reaction. What are the factors that favour the oxidative addition reaction ?

3. Answer ***any three*** questions from the following : 2×3=6

(a) Define ground term. Identify the ground terms for the free ions V^{3+} and Cr^{3+}.

(b) What are the major differences between Orgel and Tanabe-Sugano diagram ?

(c) The complex that would show paramagnetic behavior is

(i) $[MnO_4]^-$

(ii) $[FeCl_4]^-$

(iii) $[Cu(1,10-phen)_2]^+$

(iv) $[Fe(CN)_6]^{4-}$

(d) The expected spin-only magnetic moments for $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ respectively are

(i) 1·73 and 1·73 B.M.

(ii) 1·73 and 5·92 B.M.

(iii) 0·0 and 1·73 B.M.

(iv) 0·0 and 5·92 B.M.

Or

Answer the following questions :

(a) The magnetic moments of Co(II) tetrahedral complexes lie in the range of 4·4–4·8 BM, whereas those of octahedral complexes are 4·8–5·2 B.M. at room temperature. Explain. 3

Contd.

(b) An aqueous solution of $[Fe(H_2O)_6]^{2+}$ shows an absorption spectrum consisting of a single band that splits into two components at ~10·400 and ~8·300 cm^{-1}. Explain the spectrum with the necessary diagram. 2

(c) The compound which shows $M \rightarrow L$ charge transfer is – 1

(i) $Ni(CO)_4$

(ii) $K_2Cr_2O_7$

(iii) HgO

(iv) $\left[Ni(H_2O)_6\right]^{2+}$

UNIT–III

(Marks : 29)

(A)

(Marks : 07)

4. Answer ***any two*** questions from the following : 3·5×2=7

(a) Mention significance of spin-spin coupling in NMR spectroscopy. Draw ^1H and ^{31}P NMR spectra of $(CH_3)_2PH$ molecule. 1+1·5+1=3·5

(b) Explain spin-spin and spin-lattice relaxation in NMR spectroscopy. Why solid-slate NMR is usually broad in nature compared to liquid-state NMR ? 2+1·5=3·5

(c) (i) How can you distinguish *fac*– and *mer*– $\left[RhCl_3(PPh_3)_3\right]$ with the help of ^{31}P NMR spectroscopy ? 2

(ii) Write short note on NMR shift reagent. 1·5

(B)

(Marks : 07)

5. Answer ***any two*** questions from the following : 3·5×2=7

(a) Water is not a suitable solvent for the ESR experiment, why ? What are the factors which affect the value of g ? 2·5+1=3·5

(b) Explain super hyperfine splitting with one suitable example. Predict the number of lines exhibited by a high-resolution EPR spectrum of the species $\left[Cu(en)_2\right]^{2+}$. [$I_{Cu}$=3/2 and that of N=1]. 2·5+1=3·5

(c) What is Kramer's doublet? For a tetragonally distorted Cr(III) complex, zero-field splitting results in the following numbers of Kramer's doublets: 2·5+1=3·5

(i) One

(ii) Two

(iii) Three

(iv) Four

(d) Spectrum of a single crystal of Mn^{2+} doped into MgV_2O_6, showing five allowed transitions, each again splits to six lines ($Mn = I = 5/2$). Explain the spectral pattern. Draw the ESR spectrum of an aqueous solution of $CuSO_4.5H_2O$ at room temperature. 2·5+1=3·5

(C)

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6. Answer ***any two*** of the following questions: 3×2=6

(a) Explain the concept of isomer shift in Mössbauer spectroscopy and how it relates to oxidation state and electronic environment of iron nucleus ?

(b) What is recoil energy ? A Mössbauer source emits gamma rays with an energy of 14·4 *keV*. The mass of the emitting nucleus is $2{\cdot}3\times10^{-25}kg$. Calculate the recoil energy of the nucleus when it emits the gamma photon. 1+2=3

(c) What is the electric quadrupole moment? How does the quadrupole moment affect the hyperfine splitting observed in Mössbauer spectra ? 1+2=3

(d) How do spin state and ligand symmetry affect the isomer shift/Mössbauer spectra ? In which of the following complexes quadruple splitting is possible and why ? 2+1=3

$SnCl_4$, SnF_4, SnI_4, $SnBr_4$

(D)

(Marks : 05)

7. Write the basic principle of nuclear quadruple resonance (NQR) spectroscopy. Provide examples of molecules/nuclei with different nuclear quadruple moment. 2+1=3

Or

Why is NQR spectroscopy referred to as zero-field NMR spectroscopy ? Explain the correct increasing order of ^{35}Cl QCC (quadrupole coupling constant) values for *Cl–C*, *Cl–F*, *Cl–Cl* and *Cl–Si* bonds. 1+2=3

8. The NQR frequency for a nucleus with I = 3/2 in an axially symmetric EFG is 100 *MHz*. Calculate e^2Qq/h. 2

(E)

(Marks : 04)

9. Give the principle of photoelectron spectroscopy (PES) briefly. What are the differences between XPES and UVPES spectroscopy ? 2+2=4

UNIT–IV

(Marks : 07)

10. Answer the following questions :

(a) Define the term intensity of magnetization, magnetic permeability and magnetic susceptibility. 3

Or

Show how magnetic susceptibility varies with temperature for paramagnetic, ferromagnetic and diamagnetic compound. Define the Neel temperature (T_N) and Curie temperature (T_C). 1+2=3

(b) Comment on the contributions of the *orbital magnetic moment* for the following species : 1+1=2

(i) d^4 (high spin)

(ii) d^7 (high spin)

(c) $\mu_{obs}(\mu_{eff})$ of a Co^{2+} octahedral complex may be as high as 5·2 B.M. Explain. 2

Or

Explain the spin-crossover diagrammatically taking a suitable example.

Total number of printed pages–11

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2024

(December)

CHEMISTRY

Paper : 301

(Core Course)

(Inorganic Chemistry–III)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

UNIT–I

(Marks : 08)

1. Answer ***any four*** of the following questions : 2×4=8

   (a) Why is there often a discrepancy between the theoretical (calculated) magnetic moment and the experimental magnetic moment of Eu^{3+} ions ?

(b) With the help of a suitable example describe the mechanism by which lanthanide shift reagents (LSRs) induce shifts in the NMR spectra of organic molecules.

(c) Why do actinides exhibit a greater range of oxidation states than lanthanides, and how does this influence their chemical behavior ?

(d) What is elution time in chromatography ? Compare the elution times of La^{3+} and Lu^{3+} ions and discuss the factors contributing to any differences observed. 0.5+1.5=2

(e) Why the lanthanide contraction occurs ? How does it affect the properties of 4d and 5d series transition metals ? 1+1=2

(f) Compare the spectral properties of lanthanides and actinides.

UNIT–II

(Marks : 16)

2. Answer the following questions :

(a) What is Effective Atomic Number (EAN) rule for coordination compound ? Mention if the following compounds obey 18-electron rule or not ? Give reason. 1+3=4

(i) $\left[Ir(CO)Cl(PPh_3)_2\right]$;

(ii) $\left[IrBr_2(CH_3)(CO)(PPh_3)\right]$

Or

Write bnief notes on : 2+2=4

(i) Irving-William order of stability of metal complexes and its significance.

(ii) Relation between stepwise and overall stability constant.

(b) Answer *any three* questions of the following : 2×3=6

(i) What are the conditions for two fragments to be isolobal ? How do you account the isolobality of $Mn(CO)_5$ with CH_3 and Cl.

Contd.

(ii) Discuss the reactivity of carbonyl ligand with reference to various chemical reactions.

(iii) Discuss how the following factors affect the magnitude of C–O stretching frequencies (ν_{CO} cm^{-1}) in various metal carbonyls. 1+1=2

(a) Charge on metal center

(b) Presence of other ligands.

(iv) What are fluxional molecules. Give examples.

(v) With suitable example define oxidative addition and reductive elimination reaction. What are the factors that favour the oxidative addition reaction ?

3. Answer ***any three*** questions from the following : 2×3=6

(a) Define ground term. Identify the ground terms for the free ions V^{3+} and Cr^{3+}.

(b) What are the major differences between Orgel and Tanabe-Sugano diagram ?

(c) The complex that would show paramagnetic behavior is

(i) $[MnO_4]^-$

(ii) $[FeCl_4]^-$

(iii) $[Cu(1,10-phen)_2]^+$

(iv) $[Fe(CN)_6]^{4-}$

(d) The expected spin-only magnetic moments for $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{3-}$ respectively are

(i) 1·73 and 1·73 B.M.

(ii) 1·73 and 5·92 B.M.

(iii) 0·0 and 1·73 B.M.

(iv) 0·0 and 5·92 B.M.

Or

Answer the following questions :

(a) The magnetic moments of Co(II) tetrahedral complexes lie in the range of 4·4–4·8 BM, whereas those of octahedral complexes are 4·8–5·2 B.M. at room temperature. Explain. 3

(b) An aqueous solution of $[Fe(H_2O)_6]^{2+}$ shows an absorption spectrum consisting of a single band that splits into two components at ~10·400 and ~8·300 cm^{-1}. Explain the spectrum with the necessary diagram. 2

(c) The compound which shows $M \rightarrow L$ charge transfer is – 1

(i) $Ni(CO)_4$

(ii) $K_2Cr_2O_7$

(iii) HgO

(iv) $\left[Ni(H_2O)_6\right]^{2+}$

UNIT–III

(Marks : 29)

(A)

(Marks : 07)

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