

Total number of printed pages-8

1 (Sem-3/FYUGP) CHE41MJ

2025

CHEMISTRY

(Major)

Paper : CHE4300104 MJ

(Chemistry-III)

Full Marks : 45

Time : 2 hours

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

1. Choose the correct option from the following questions : 1×5=5

(a) The species responsible for the superacidity of $SbF_5 - HSO_3F$ system is

(i) HSO_3F

(ii) SbF_5

(iii) HF

(iv) $H_2SO_3F^+$

(b) The complexes

$[Pt(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$ respectively are

- (i) Paramagnetic, Paramagnetic
- (ii) Diamagnetic, Diamagnetic
- (iii) Paramagnetic, Diamagnetic
- (iv) Diamagnetic, Paramagnetic

(c) Which of the following species is aromatic according to Hückel's rule?

- (i) Cyclobutadiene
- (ii) Cyclopentadienyl anion
- (iii) Cyclooctatetraene
- (iv) Cyclopentadienyl cation

(d) According to Raoult's law, the partial vapour pressure of a component in an ideal solution is directly proportional to :

- (i) Its mole fraction in the vapour phase
- (ii) Its mole fraction in the liquid phase
- (iii) Total pressure of the solution
- (iv) Temperature of the system

(e) Consider this assertion-reason statement :

Assertion (A) : Aniline does not undergo Friedel-Craft alkylation easily.

Reason (R) : The diazonium salts of aromatic amines are more stable than those of aliphatic amines.

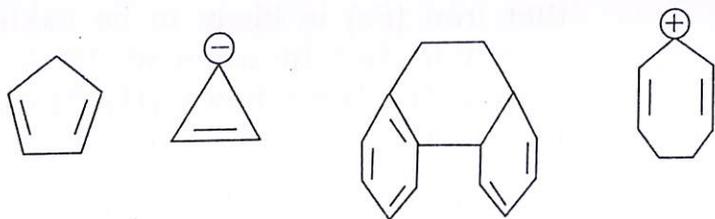
Which one of the following is correct?

- (i) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (ii) Both (A) and (R) are true and (R) is not the correct explanation of (A).
- (iii) (A) is true, but (R) is false.
- (iv) Both (A) and (R) are false.

2. Answer **any five** from the following questions : 2×5=10

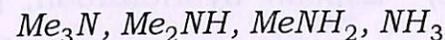
- (a) Predict which compound is more acidic, H_2SO_4 or H_2SeO_4 and justify your answer.
- (b) Taking overpotential into account show that iron (Fe) is likely to be oxidized rapidly to Fe^{2+} by water at 25°C.
(Given $Fe^{2+}/Fe = 0.44V$ [$H_2(P) = 1bar$]
[$Fe^{2+}] = 1mol.$)
- (c) State Raoult's law and Henry's law.

- (d) How alcohols can be prepared from alkene? Give equations only.
- (e) Explain the physical significance of fugacity.
- (f) Why is cyclopentadiene ($K_a = 10^{-15}$) much more acidic than 1,3-cyclohexadiene?
- (g) What are the limitations of Valence Bond theory of co-ordination compounds?
- (h) How can you distinguish between aldehydes and ketones by oxidation reactions?
- (i) How the nature of solvent affects the rate of nucleophilic substitution reaction?
- (j) Classify the following compounds as aromatic, antiaromatic or non-aromatic: $\frac{1}{2} \times 4 = 2$



3. Answer **any four** from the following questions : $5 \times 4 = 20$

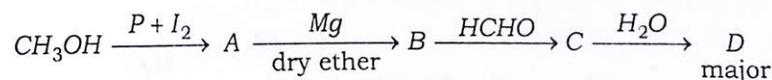
- (a) In aqueous solution, arrange the basicities of the following amines and justify your answer : $2 + 3 = 5$



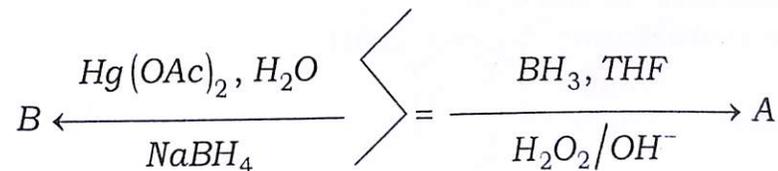
- (b) Discuss the principle of redox titration. Why HCl is not used in redox titration? $4 + 1 = 5$

- (c) Explain why vapour pressure of a solvent decreases when a non-volatile solute is added. The vapour pressure of pure benzene at 25°C is 100mm Hg . When 2.0g of a non-volatile solute (molar mass = 120g mol^{-1}) is dissolved in 78.0g benzene, calculate the vapour pressure of the solution. $2 + 3 = 5$

- (d) (i) Find the A, B, C and D : $\frac{1}{2} \times 4 = 2$



- (ii) Find out the major products of following reactions : 2



(iii) A molecule with 10π electrons in a conjugated, cyclic and flat system will be aromatic. 1

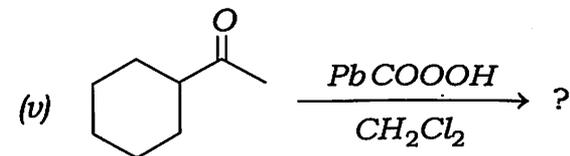
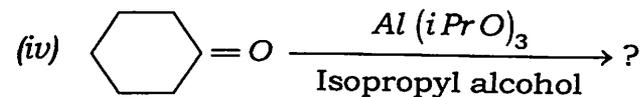
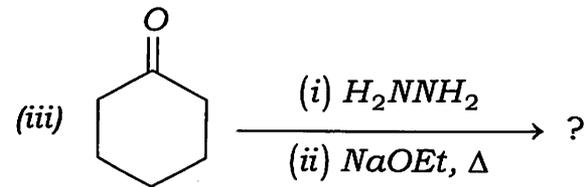
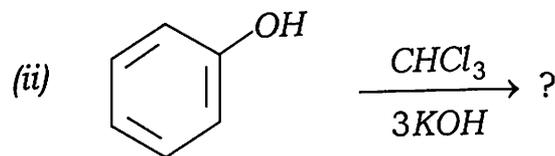
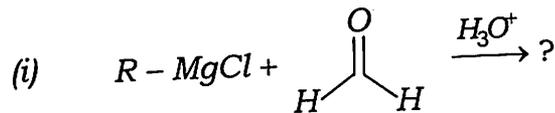
(State True or False)

(e) Explain hybridization, geometry and magnetic properties of $[\text{Co}(\text{CN})_6]^{3-}$ on the basis of Valence Bond theory.

(f) Write one preparation reaction of PCC. How PDC is advantageous over PCC? 3+2=5

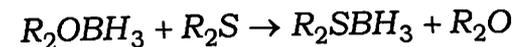
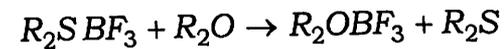
(g) Discuss the dependence of partial molar Gibbs free energy on mole fraction in a binary mixture. Draw the μ - x diagram for ideal and non-ideal mixtures. 3+2=5

(h) Write the products of the following reaction : 1×5=5



4. Answer **any one** from the following questions : 10×1=10

(a) (i) What is symbiosis? Explain the following reactions in terms of symbiosis : 1+2=3



(ii) What is proton sponge? Give one example. 2

(iii) Write the postulates of Valence Bond theory of coordination complexes. What are inner orbital and outer orbital complexes? Give one example each. 3+2=5

- (b) (i) Establish Rault's law for a completely miscible liquid pair. Show graphically how the vapour pressure of a completely miscible liquid pair changes with the composition of the mixture. 3+2=5
- (ii) What do you mean by activity of a substance? Show that $G + G^\circ + RT \ln a$. 2+3=5
- (c) (i) Derive Gibbs-Duhem Equation. 3
- (ii) What are abnormal colligative properties? 2
- (iii) How do you differentiate 1°, 2°, 3° alcohols? Give chemical reactions. 5
- (d) (i) What are magic acids? Give one example. 1+1=2
- (ii) Define levelling effect. How it helps in discrimination of strength of various acids? 1+2=3
- (iii) Write short notes on the following topics : **(any two)** 2½×2=5
- (i) Hückel's rule
- (ii) Benzyne mechanism
- (iii) Oppenauer oxidation
- (iv) Concept of chemical potential
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Total number of printed pages-11

1 (Sem-3/FYUGP) CHE42MJ

2025

CHEMISTRY

(Major)

Paper : CHE4300204 MJ

(Molecular Spectroscopy-1)

Full Marks : 45

Time : 2 hours

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

Answer **either** in English **or** in Assamese.

1. Answer the following questions : 1×5=5

তলৰ প্ৰশ্নবোৰৰ উত্তৰ লিখা :

(i) Which type of molecule shows pure rotational spectra ?

কেনেধৰণৰ অণুৱে শুদ্ধ ঘূৰ্ণনীয় বৰ্ণালী প্ৰদৰ্শন কৰে?

(ii) Name a factor affecting population of energy levels.

শক্তিস্তৰৰ জনসংখ্যা প্ৰভাৱিত কৰা এটা কাৰকৰ নাম লিখা।

(iii) Name *one* molecule that is IR inactive but Raman active.

এটা IR নিষ্ক্রিয় কিন্তু ৰমন সক্ৰিয় অণুৰ নাম লিখা।

(iv) What is meant by photosensitizer? Name a photosensitizer used in photochemical reaction.

আলোক সংবেদনশীলতা মানে কি? আলোক-ৰাসায়নিক বিক্ৰিয়াত ব্যৱহাৰ হোৱা এটা আলোক সংবেদনশীলতাৰ নাম লিখা।

(v) Which type of light source is commonly used in Raman spectroscopy?

সাধাৰণতে ৰমন স্পেকট্ৰোস্কোপিত কেনেধৰণৰ পোহৰৰ উৎস ব্যৱহৃত হয়?

2. Answer *any five* of the following questions :

2×5=10

তলত দিয়া প্ৰশ্নবোৰৰ যিকোনো পাঁচটাৰ উত্তৰ লিখা :

(i) What are auxochromes? Give some examples.

সহবৰ্ণক কি? কিছুমান উদাহৰণ দিয়া।

(ii) What is quantum yield? Give the causes of high and low quantum yield of photochemical reaction.

কোৱাণ্টাম ইল্ড কি? উচ্চ আৰু নিম্ন কোৱাণ্টাম ইল্ডৰ কাৰণ দিয়া।

(iii) Write mutual exclusion principle.

পাৰস্পৰিক বৰ্জন নীতি লিখা।

(iv) How does hydrogen bonding affect the IR spectra?

হাইড্ৰ'জেন বান্ধনিয়ে IR বৰ্ণালীৰ ওপৰত কেনেধৰণৰ প্ৰভাৱ পেলায়?

(v) Explain why polyenes show absorption in the visible region?

বহুযোগীসমূহে কিয় দৃশ্যমান অঞ্চলত শোষণ দেখুৱায়?

(vi) What is selection rule of IR spectroscopy?

IR বৰ্ণালীবিজ্ঞানত বাচনিৰ নিয়ম কি?

(vii) Explain the reason for the colour of nitro and azo compounds.

নাইট্ৰ' আৰু এজ' যৌগবোৰৰ ৰঙীন হোৱাৰ কাৰণ ব্যাখ্যা কৰা।

(viii) The incident light has a wavelength of 4358Å and the scattered light is observed at 4477Å. Calculate the Raman shift in cm^{-1} .

এটা আপতিত ৰশ্মিৰ তৰংগদৈৰ্ঘ্য 4358Å আৰু বিকিৰিত ৰশ্মিৰ তৰংগদৈৰ্ঘ্য 4477Å। cm^{-1} ত ৰমন সিফ্ট গণনা কৰা।

(ix) Calculate the energy associated with (i) one quantum (ii) one Einstein. Given that the wavelength of radiation is 7500Å ($h = 6.62 \times 10^{-27} \text{ erg sec}$, $c = 3 \times 10^{10} \text{ cm/sec}$, $1 \text{ cal} = 4.184 \times 10^7 \text{ ergs}$).

(i) এটা কোৱাণ্টামৰ সৈতে জড়িত শক্তি আৰু (ii) এটা আইনষ্টাইনৰ সৈতে জড়িত শক্তি গণনা কৰা। বিকিৰণৰ তৰংগদৈৰ্ঘ্য দিয়া আছে 7500Å।
($h = 6.62 \times 10^{-27} \text{ erg sec}$,
 $c = 3 \times 10^{10} \text{ cm/sec}$,
 $1 \text{ cal} = 4.184 \times 10^7 \text{ ergs}$)

(x) Using IR spectra, how will you distinguish between (i) ethanol and ethanal (ii) acetone and acetic acid?

IR বৰ্ণালীৰ সহায়ত কেনেকৈ তুমি (i) ইথানল আৰু ইথানেল (ii) এচিটন আৰু এচেটিক এচিদৰ মাজত পাৰ্থক্য কৰিবলৈ পাৰিবা?

3. Answer **any four** of the following questions :

5×4=20

তলৰ যিকোনো চাৰিটাৰ উত্তৰ লিখা :

(i) (a) Discuss the various factors affecting the intensity of spectral lines. 3

বৰ্ণৰেখাৰ তীব্রতাক প্ৰভাৱিত কৰা কাৰকসমূহ আলোচনা কৰা।

(b) What is hypsochromic shift? 2

হিপছ'ক্রমিক সিফ্ট মানে কি?

(ii) Write short notes on : $2\frac{1}{2} \times 2 = 5$

চমু টোকা লিখা :

(a) Wave-particle duality

তৰংগ-কণিকাৰ দ্বৈততা

(b) Absorption cross-section and Einstein coefficients

অৱশোষণ প্ৰস্থচ্ছেদ আৰু আইনষ্টাইনৰ সহগ

(iii) (a) State basic principle of the Woodward-Fieser rule. 2

উডৱাৰ্ড-ফিচাৰৰ নিয়মৰ মৌলিক নীতি কি?

(b) Calculate the λ_{max} for 1,3-butadiene using the Woodward-Fieser rules. 3

উডৱাৰ্ড-ফিচাৰৰ নিয়ম ব্যৱহাৰ কৰি 1,3 বিউটাডাইনৰ λ_{max} গণনা কৰা।

(iv) Explain the Franck-Condon principle. Discuss its significance in electronic spectra with the help of a potential energy diagram.

ফ্ৰাংক-কণ্ডন নীতি ব্যাখ্যা কৰা। বিভিন্ন শক্তিৰ ৰেখাচিত্ৰৰ সহায়ত ইয়াৰ ইলেক্ট্ৰনীয় বৰ্ণালীৰ তাৎপৰ্য আলোচনা কৰা।

(v) Derive energy expression for vibrational Raman spectra.

কম্পনজনিত ৰমন বৰ্ণালীৰ শক্তি সমীকৰণ উপপাদন কৰা।

(vi) (a) What are the different factors that contribute to the width of spectral lines? 3

বৰ্ণৰেখাৰ প্ৰস্থক বৰঙণি যোগোৱা বিভিন্ন কাৰকসমূহ কি কি?

(b) Assume that a molecule undergoes spectroscopic transition from ground state to an excited state where its lifetime is 10^{-4} s. Calculate approximate uncertainty in excited state energy level and width of the spectral line in Hz. 2

এটা অণুৱে ভূমি অৱস্থাৰ পৰা উত্তেজিত অৱস্থালৈ এটা স্পেক্ট্ৰ'স্কপিক ৰূপান্তৰ কৰে বুলি ধৰা যাওঁক য'ত উত্তেজিত অৱস্থাৰ আয়ুস 10^{-4} ছেকেণ্ড। উত্তেজিত অৱস্থাৰ শক্তিৰ অনিশ্চয়তা আৰু বৰ্ণালী ৰেখাৰ প্ৰস্থ (Hz)ত গণনা কৰা।

(vii) (a) The infrared spectrum of an organic compound with molecular formula C_7H_5N shows prominent bands at 3060cm^{-1} , 2250cm^{-1} , 1600cm^{-1} , 1580cm^{-1} , 1500cm^{-1} , 1450cm^{-1} , 750cm^{-1} and 700cm^{-1} . What should be the probable structure of the compound? 3

এটা জৈব যৌগৰ C_7H_5N , ইনফ্ৰাৰেড বৰ্ণালীয়ে $3060cm^{-1}$, $2250cm^{-1}$, $1600cm^{-1}$, $1580cm^{-1}$, $1500cm^{-1}$, $1450cm^{-1}$, $750cm^{-1}$ আৰু $700cm^{-1}$ ত বিশিষ্ট বেণ্ড দেখুৱায়। যৌগটোৰ সম্ভাৱ্য গঠন কি হব?

(b) What is the change in the rotational constant B when hydrogen is replaced by deuterium in the hydrogen molecule? 2

হাইড্ৰ'জেন অণুত হাইড্ৰ'জেনক ডিউটেৰিয়ামৰ দ্বাৰা পৰিবৰ্তন কৰিলে ঘূৰ্ণন ধ্ৰুৱক B -ৰ পৰিবৰ্তন কেনেকুৱা হব?

(viii) State the Beer-Lambert law. Write mathematical form of Beer-Lambert law. What are the limitations of Beer-Lambert law? 2+1+2=5

বিয়ৰ-লেম্বাৰ্ট সূত্ৰটো লিখা। বিয়ৰ-লেম্বাৰ্ট সূত্ৰৰ গাণিতিক ৰূপ লিখা। বিয়ৰ-লেম্বাৰ্ট সূত্ৰৰ সীমাবদ্ধতাসমূহ কি কি?

4. Answer **any one** of the following questions: 10

তলৰ যিকোনো এটা প্ৰশ্নৰ উত্তৰ লিখা :

(i) What do you mean by Raman effect? Explain Rayleigh scattering, Stokes and anti-Stokes lines. Why Stokes lines are more intense than anti-Stokes lines? 3+6+1=10

ৰমন প্ৰভাৱৰ মানে কি বুজা? ৰেলি বিচ্ছুৰণ, ষ্টোক্‌স ৰেখা আৰু এন্টিষ্টোক্‌স ৰেখাৰ বৰ্ণনা কৰা। ষ্টোক্‌স ৰেখা কিয় এন্টিষ্টোক্‌স ৰেখাতকৈ বেছি তীব্ৰ হয়?

(ii) (a) Explain how IR spectroscopy is used for the elucidation of molecular structure. Give suitable examples. 5

কেনেদৰে IR স্পেক্ট্ৰ'স্কোপি আণৱিক গঠনত ব্যৱহৃত হয় বিশদভাৱে ব্যাখ্যা কৰা। উপযুক্ত উদাহৰণ দিয়া।

(b) What do you understand by degrees of freedom? Calculate and explain diagrammatically the different normal modes of vibration of H_2O molecule. 1+4=5

অণু এটাৰ স্বাধীনতাৰ মাত্ৰা বুলিলে কি বুজা? H_2O অণুৰ সাধাৰণ সঞ্চাৰণৰ প্ৰকাৰ কিমানটা নিৰ্ণয় কৰা আৰু চিত্ৰ আঁকি বুজাই দিয়া।

- (iii) Construct the Jablonski diagram to illustrate the following concepts of molecular emission spectroscopy—
 (a) internal conversion (b) vibration relaxation (c) intersystem crossing (d) fluorescence (e) phosphorescence.

তলত দিয়া আণৱিক নিঃসৰণ, স্পেক্ট্ৰ'স্কোপিক ধাৰণাসমূহ বহলাই লিখিবলৈ জেবলনস্কি চিত্ৰ গঠন কৰা—

- (a) আভ্যন্তৰীণ ৰূপান্তৰ (b) কম্পন শিথিলতা
 (c) ইন্টাৰছিষ্টেম ক্ৰছিং (d) ফ্ল'ৰেচেন্স (e) ফছফোৰেচেন্স।

- (iv) (a) Discuss the consequences of the Born-Oppenheimer approximation in molecular spectroscopy. 5

আণৱিক স্পেক্ট্ৰ'স্কোপিক বৰ্ণ-অপেনহাইমাৰ অনুমানৰ ফলাফল আলোচনা কৰা।

- (b) Show that for a rotational spectrum of a diatomic molecule, the rotational quantum number (to the nearest integer value) for the maximum populated level is given by

$$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \quad 5$$

দেখুওৱা যে—
 দ্বি-পাৰমাণৱিক অণু এটাৰ ঘূৰ্ণন বৰ্ণালীৰ ক্ষেত্ৰত সৰ্বোচ্চ অধিকৃত স্তৰ এটাৰ ঘূৰ্ণন কোৱাণ্টাম সংখ্যাৰ মান (নিকটতম অখণ্ড সংখ্যাৰ হিচাপত)

$$J_{max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$