RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER EXAMINATION, JULY 2021
THIRD YEAR [BATCH 2018-21]
CHEMISTRY (HONOURS)
Paper : VIII

Date : 10/07/2021
Time : 11.00 am - 3.00 pm
Full Marks : 100

Group - A

Attempt **one question** from each unit

Unit - I

1) a) Why generally the phosphorescence intensity increases as temperature is lowered or solvent viscosity increased? (3)

b) Emission spectra is generally studied for electronic transition, rarely for vibrational transitions, almost never for a rotational transition. Explain. (3)

c) Explain (with the help of a schematic diagram depicting the relevant transitions) why fluorescent emission wavelength is generally independent of the excitation wavelength. (3)

d) The quantum yield for the photodissociation of ICN(g) into I(g) and CN(g) by a 306 nm pump pulse is 1.00. If the radiant energy of the pump pulse is 1.55 x 10^{-4} J, determine the number of CN(g) radicals created per pulse if only 0.1 % of the incident light is absorbed by the ICN (g) sample. (4)

2) a) Photosensitizers essentially act as catalysts for a reaction. Explain. (3)

b) With the aid of an energy diagram for a diatomic molecule, show how an electronic transition may lead to a bond breaking. (3)

c) Upon absorption of 313 nm light, acetone photodissociates according to the chemical equation

$$(\mathrm{CH_3})_2\mathrm{CO} + h\nu \longrightarrow \mathrm{C_2H_6}(g) + \mathrm{CO}\ (g)$$

Exposure of a gaseous sample of acetone to a radiant power pf 1.71 x 10^{-2} W at 313 nm for a period of 1.15 x 10^{4} s results in the photodissociation of 8.68 x 10^{-5} mol of acetone. Determine the quantum yield for this photodissociation reaction. Also answer the following questions

i) Does the result in any way violate the Einstein's law of photochemical equivalence?

ii) What is the assumption that you made to arrive at the result? (3+2+2)

Unit - II

3) a) A hypothetical quantum mechanical system has the energy levels E = an(n+4), where n = 0, 1, 2,… and 'a' is a positive constant. The selection rule for the radiative transitions is $\Delta n = \pm 3$. Find out the formula for the allowed absorption frequencies in terms of n_{lower}, a and h. For a collection of such systems, distributed among many energy levels, the lowest frequency absorption transition is observed at 80 GHz. What is the next lowest absorption frequency? (2+2)

b) The J = 0 →1, v = 0 →0, transition for $^{1}H^{79}Br$ occurs at 500.7216 GHz and that for $^{1}H^{81}Br$ occurs at 500.5658 GHz. Calculate

i) the bond distance R_0 in each of these molecules. [Neglect the centrifugal distortion] How much realistic the results you have observed? Comment.

ii) Predict the J = 1 →2, v = 0 →0 transition frequency for $^{1}H^{79}Br$. (3+2)

c) Use the concept of semi-classical theory to explain the appearance of Rayleigh scattering as well as the Stokes and anti-Stokes lines. Give an analytical treatment, using a representative diagram of excitations for respective lines. (3)

4) a) AB_2 is a molecule with no dipole moment and is having a plane of symmetry. Which among the Microwave, IR and Raman spectra will be observed for the above molecule? Why? Also mention the two selection rules for these spectral transitions. (4)

b) State true or false with explanation for the followings. (2×2)

i) C-C and C=C bonds are of comparable stretching frequencies observed in IR spectra.

ii) No vibrational-Raman line corresponding to an IR active line confirms that the molecule is a centro-symmetric one.

c) Provided the higher order terms are neglected for the vibrational wavenumbers of an anharmonic oscillator, the equation

$$\Delta\tilde{G}(v) = \tilde{\nu} - 2(v+1)x_e\tilde{\nu}$$

is the acceptable equation for the IR spectral transition. Use the following data for CO to determine the values of $\tilde{\nu}$ and $x_e\tilde{\nu}$.

v	0	1	2	3	4
$\Delta\tilde{G}(v)$/cm	2143.1	2116.1	2088.9	2061.3	2033.5

Also comment on the positions of lines of CO, if the vibrational lines are to observe. (4)

Group - B

Attempt **one question** from each unit

Unit - III

5) a) Explain the mechanism of osazone formation with special reference to Amadori rearrangement. Why osazone formation does not proceed beyond the first two carbon atoms? (2+1)

b) What is anomeric effect? In dry methanol “α” – and “β” (+)D-glucose exist in equal amount? (1+2)

c) E, F and G are three aldohexoses. E and F yield D-Sorbitol when they are catalytically hydrogenated. E and F yield different osazones with Ph-NH-NH_2. F and G give the same osazones but different alditols. Give the structures of E, F and G assuming that F and G are D-aldohexoses. (3)

d) Show the reaction steps and the mechanism involved in N-terminal amino acid determination by Edman method. (2)

e) Get adenosine from its triphosphate. (1)

f) Write the different interactions responsible for stabilizing the secondary structure of protein. (1)

g) Explain the Isoprene rule with a suitable example? (2)

6) a) Convert: $\alpha-D-$glucopyranose to 2,4-di-O-methyl-D-glucopyranose. (2)

b) Explain the formation of the products, when D-glucose is separately allowed to react with acetone / dry HCl and benzaldehyde / dry HCl. (2)

c) Justify or Criticize: Mutarotation of $\delta-$Gluconolactone is not a case of first order asymmetric transformation. (2)

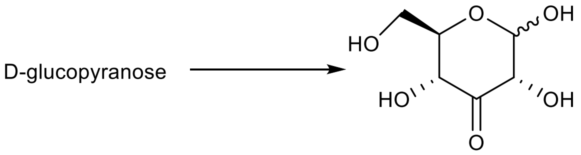
d) Utilizing the structural illustration, explain the non-reducing property of Sucrose. (2)

e) Using chemical reactions justify the importance of the following reagents in peptide sequence analysis: (1.5+1.5)

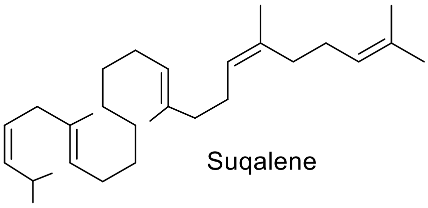
   i) Ph-N=C=S

   ii) Br-CN

f) Convert: (2)



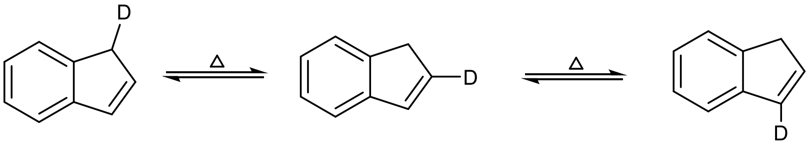
g) Indicate the nature of head-tail combination present in the following molecules: (2)



Suqalene

Unit - IV

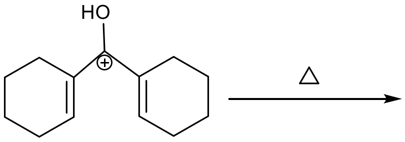
7) a) Explain the following observation: (2)



b) Predict the product(s) in each of the following reaction with stereochemistry: (E,E)-CH_3-CH=CH-O-CH_2-CH=CH-CH_3 (3)

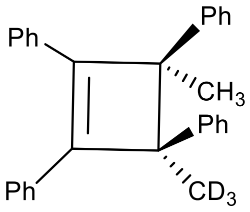
c) [1,3] sigmatropic shift is difficult to achieve thermally. Explain the phenomenon using F.M.O approach. (2)

d) Show the course of the following pericyclic reaction with stereochemistry. (2)

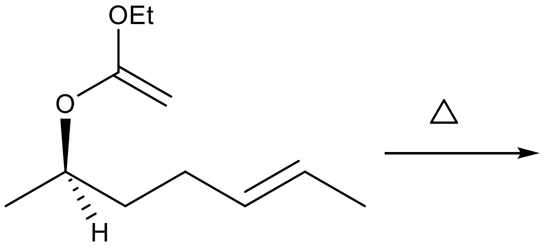


e) Give one suitable use for the reagent: TMSI (1)

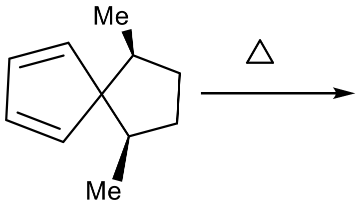
8) a) How would you employ the pericyclic reactions in the synthesis of the following and also explain the reaction with FMO approach. (3)



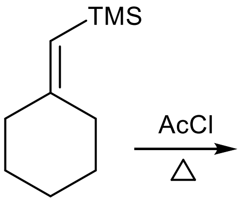
b) Predict the product(s) in the following reaction showing the sterochemistry and indicate the reaction pathways : (2)



c) Predict the product(s) in the following reaction and also indicate the reaction pathways: (2)



d) Predict the product for the following reaction and also explain with suitable mechanism: (2)



e) Give one suitable synthetic use for the reagent: TMSCN (1)

Group - C

Attempt **one question** from each unit

Unit - V

9) a) M-M binding energy (ΔH_{at}) has been found to be highest for V ($3d^3 4s^2$) in place of Cr ($3d^5 4s^1$) and lowest for Zn ($3d^{10} 4s^2$)-why? (2)

b) What happens, with reaction(s), when chromate solution ($pH \geq 8$) is acidified to $pH = 2$ to 4 and treated with Pb(II) solution stating the species those are in equilibriums. (2)

c) Uranium(VI) chemistry is dominated by uranyl ion (UO_2^{2+})-why? (2)

d) In the cation-exchange method of separation of 4f-block metal ions from their aqueous mixture, explain the loading order of the metal ions over resin bed and sequence of their release from the resin bed surface using a suitable eluant. (3)

10) a) Depict graphically the variation of third ionization enthalpy (ΔI_3) of 3d- block elements, Sc-Zn explaining the anomaly, if any. (2)

b) Compare the chemistry of MCl_4 (M = Ti, Zr and Hf) in the light of volatility and hydrolytic behavior.

(2)

c) Why is the magnetic moment of Eu(III)-compounds differed noticeably from that of experimental value when calculated using the relation, $\mu_J = g_J [J(J+1)]^{0.5}$ relation? (2)

d) List the uncommon oxidation states of Fe, Co and Ni citing acompound against of each state. How is the specified sate in mentioned compound stabilized? (3)

Unit - VI

11) a) Symmetrical di-μ-hydroxotetrakis(ethylenediamine)dicobalt(III)chloride (A) reacts with aq. HCl to give a product $Co(en)_2Cl_3$ (B) which is resolvable with optical isomers. When it is kept in acidic solution, the compound changes colour and gives an isomer (C) which is not resolvable. Give structures of (A), (B) and (C) and also write the optical isomers of (B) (3)

b) Palladium (II) and gold (III) can be determined simultaneously by reaction with methiomeprazine ($C_{19}H_{24}N_2S_2$). The absorption maximum for the Pd complex occurs at 480 nm, while that for the Au complex is at 635 nm. Molar absorptivity for Pd and Au complexes are $3.55\text{x}10^3$ and $2.96\text{x}10^3$ at 480 nm and at 635 nm $5.64\text{x}10^2$ and $1.45\text{x}10^4$ respectively. A 25.0-mL sample was treated with an excess of methiomeprazine and subsequently diluted to 50.0mL.Calculate the molar concentrations of Pd (II) and Au (III) in the sample if the diluted solution had an absorbance of 0.533 at 480 nm and 0.590 at 635 nm when measured in a 1.00-cm cell. (3)

c) $[Ni(en)_3]^{2+}$, where en= ethylenediamine, is nearly 10^6 more stable than $[Ni(NH_3)_6]^{2+}$ though both can be derived from $[Ni(H_2O)_6]^{2+}$ complex. Explain the stability of the former from thermodynamic consideration. (2)

12) a) The percentage transmittance of a transition metal complex at 360 nm and at 25˚C is 25% for a $6\text{x}10^{-4}$ mol Lit^{-1} solution in a 1 cm cell. Calculate the molar absorption coefficient in the unit of $Lmol^{-1}cm^{-1}$.(2)

b) A Compound $[Co(en)_2(NO_2)_2]Cl$ exists in three isomeric forms (A), (B) and (C). (A) reacts neither with $AgNO_3$ nor with en and is optically inactive. (B) reacts with $AgNO_3$ and forms white precipitate but not reacts with en and is optically inactive. (C) is optically active and reacts with both $AgNO_3$ and en. Identify each isomer, draw their structures and give suitable reasons for your answers. (3)

c) Coordinated water molecules of a Cd(II) complex can be successively replaced by Br^-, finally to result in $[CdBr_4]^-$. In this process, the fourth equilibrium constant is observed to be higher than the third one. Explain. (2)

d) The square planar complex $[IrCl(PPh_3)_3]$ undergoes oxidative addition of Cl_2 to give the products, which are

i) Cis and trans isomers

ii) Facial and meridonial isomers

iii) Enantiomers

iv) linkage isomers (1)

Unit - VII

13) a) Predict the products of the following reaction with justification of your answer:

$$cis\text{-}\{Pt(NH_3)_2(py)_2 + 2Cl^- \rightarrow$$ (3)

b) i) Activity of nano materials is higher than that of its bulk-why?

ii) What is the difference between “Top Down” and “Bottom Up” methods of nano-particle synthesis. (1+2)

c) For the reaction, trans-$PtL_2Cl_2 + Y \rightarrow$trans-$PtL_2ClY + Cl^-$, the rate constant (k) varies as follows: (2)

	L	Y	k(10^{-3} $mol^{-1}s^{-1}$)
i)	PPh3	py	249000
ii)	SCN−	py	180

What is the mechanism of the reaction and why?

14) a) State reducing agents (at least two) those can be used for the Au-nanoparticle (Au-NP) synthesis. Outline a method of nano-goldparticle synthesis from $AuCl_3$ and mention one use of Au-NP. (3)

b) Differentiate, taking suitable example, between Labile and Inert complexes. (2)

c) Explain the terms Dissociative and Associative reaction mechanisms of complexes taking suitable example. (3)

Group - D

Attempt **one question** from each unit

Unit - VIII

15) a) What was the amount of $K_2Cr_2O_7$ in a solution if excess KI was added to 30ml of that solution and liberated I_2 consume 45·0ml of 0·1(N) $Na_2S_2O_3$ solution upto end point? (2)

b) Using masking-demasking phenomenon how could you estimate Cu^{2+} and Zn^{2+} ions in a mixture complexometrically? (3)

c) A 0·7120 gm specimen of an ore is brought into solution and all the iron content is reduced to Fe(II). The reduced solution requires 39·2 ml of 0·02M $KMnO_4$ solution for complete titration of Fe(II). Calculate the percentage of iron in the ore. (3)

16) a) Comment on potassium bi-iodate behaving as a primary standard acid. Determine its acidimetric and oxidimetric equivalent weight. (1+2)

b) Explain the role of metal ion indicators in complexometric estimation of Ca^{+2} and Mg^{+2}. (2)

c) The permanganate end point is not permanent in permanganometric titrations —Explain with reaction. (3)

Unit - IX

17) a) What is meant by co-precipitation and post precipitation? Give differences between them. (3)

b) How does the dye fluorescein act as an indicator in the titration of chloride ion with $AgNO_3$ solution? Give the mechanism. (3)

c) Give the scheme for the gravimetric estimation of PO_4^{3-}. (2)

18) a) Calculate the percentage of iron in a sample, when 0.2010 gm of iron sample was dissolved and iron was precipitated as hydroxide on further ignition and weighing gave 0.11069 gm of ferric oxide. (3)

b) Mention the components present in pyrolusite, and give the scheme for the estimation of Mn in pyrolusite. (3)

c) Which one of the common mineral acids is used for the dissolution of a sample of brass for chemical analysis? Give reason for your answer. (2)

Unit - X

19) a) The analysis of a sample of iron ore gave the following percentage values for the iron content: 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18 and 7.11. What will be the median, standard deviation, coefficient of variation and spread values respectively? (5)

b) What is Resin and how does it help in household water softening? (3)

c) Between two compounds in thin layer chromatography, what nature of the compound depicts with lower value of retention factor? (1)

20) a) How analytically one can detect and estimate small amount of mercury (Hg) in a water sample? Explain with proper example. (2)

b) What is BOD? A 10 ml sample of sewage mixed with enough water to fill a 300 ml bottle has an initial DO of 9 mg/L. To help assure on accurate test, it is desirable to have at least a 2.0 mg/L drop in DO during the 5days run and the final DO should be at least 2.0 mg/L. For what range of BOD_5 would this dilution produce the desired results? (3)

c) Predict the order of elution of Ag^+, H^+, Ba^{2+}, Al^{3+} ions in an ion-exchange chromatography filled with resin with NH_3^+ groups. Explain the sequence of which one comes first to which one comes last with proper justification. (2)

d) Define Accuracy and Precision with suitable analogy. (2)

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