RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SIXTH SEMESTER TAKE-HOME TEST / ASSIGNMENT, JULY 2020
THIRD YEAR [BATCH 2017-20]

Starting Date & Time : 02/07/2020 at 11 a.m.
CHEMISTRY (Honours)
Closing Date & Time : 03/07/2020 at 11 a.m.
Paper : VIII
Full Marks : 100

[Attempt any five questions from each group]

Group – A (Physical Chemistry) [5×5]

1. a) In a wavelength vs intensity plot depict the three phenomena: absorption, the consequent fluorescence and phosphorescence. [2]

   b) At 480 nm, the quantum yield for the production of Fe^{+2} in the photolysis of $K_3Fe(C_2O_4)_3$ in 0.05 mol L^{-1} sulphuric acid solution is 0.94. After 20 min irradiation in a cell containing 57.4 cm^3 of solution, the solution is mixed thoroughly and a 10.00 mL sample is pipetted into a 25.00 mL volumetric flask. A quantity of 1, 10-phenanthroline is added and the flask filled to the mark with a buffer solution. A sample of this solution is placed in a 1.00 cm colorimeter cell and the transmittance measured relative to a blank containing no iron. The value of $I/I_0 = 0.543$. If the molar absorption coefficient of the complex solution is 1.11×10^3 m^2 mol^{-1}, how many quanta were absorbed by the solution? What was the absorbed intensity? [3]

2. a) Explain, (with the help of a schematic diagram depicting the relevant transitions) why the fluorescent emission wavelength is generally independent of the excitation wavelength. [2]

   b) The quantum yield of CO in the photolysis of gaseous acetone ($p < 6$ kPa) at wavelengths between 250 and 320 nm is unity. After 20 min irradiation with light of 313 nm wavelength, 18.4 cc of CO (measured at 1008 Pa and 295 K) is produced. Calculate the number of quanta absorbed and the absorbed intensity in joules per second. [3]

3. A suggested mechanism for the photolysis of ozone in low energy light is:

   I. $O_3 + h\nu \rightarrow O_2 + O$

   II. $O + O_3 \rightarrow 2O_2$

   III. $O + O_2 + M \rightarrow O_3 + M$

   The quantum yield for reaction I is φ_1.

   a) Derive an expression for the overall rate of disappearance of ozone.

   b) Write the expression for the overall quantum yield for the disappearance of ozone φ_0.

   c) At low total pressure $\varphi_0 = 2$. What is the value of φ_1? [2+2+1]

4. a) Both CO_2 and H_2O are triatomic molecules. How does one distinguish them (in terms of geometry – linear or non-linear) from IR- spectroscopic study? Give a pictorial description of their bending vibrational modes. [3]

b) Justify that the J = 0 is not most populated rotational level. Explain with a rough sketch. [2]

5. a) The bond length of $^{14}N^{16}O$ is experimentally found to be 1.51×10^{-10} m. Considering the molecule as a rigid rotor rotating freely in 3D space, calculate

i) rotational energy for the lowest rotational level

ii) wavelength of the light necessary to excite the $^{14}N^{16}O$ molecule from the ground state to its 1st excited state. [2+1]

b) For a hetero-diatomic molecule, rotational-vibrational spectra are observed with P and R lines. What is the selection rule involved, if the rigid rotor-harmonic oscillator model is assumed? [2]

6. a) Justify that vibrational transitions in HCl are generally observed from v = 0 to v = 1 at room temperature (27°C) i.e. v = 0 is generally populated more than higher level. [Given the fundamental vibrational frequency is $8.66 \times 10^{13}\ S^{-1}$]. [2]

b) Explain the change in spectroscopic data, if the molecule under spectroscopic experiment is described by the energy expression

$$\Delta \in_{J\to J+1} = 2B(J+1) - 4D(J+1)^3\ cm^{-1}$$

rather than being expressed as

$$\Delta \in_{J\to J+1} = 2\mathrm{B}(J+1)\,cm^{-1}$$

Also explain the terms involved above. [3]

Group – B (Organic Chemistry) [5×5]

7. a) Population distribution of α and β-anomer of D-glucose and D-mannose is as follows:

	α-anomer	β-anomer	Medium
D-glucose	36%	64%	H_2O
D-mannose	69%	31%	H_2O

Explain this observation. [2]

b) An aldopentose [P] can be oxidized with HNO_3 to an optivally active aldaric acid. A Kiliani-Fischer synthesis starting with [P] gives two new aldoses [Q] and [R]. Aldose [Q] can be oxidized to an optically inactive aldaric acid, but aldose [R] is oxidized to an optically active aldaric acid. Assuming the D-configuration, give the structures of [P], [Q] and [R]. Justify clearly the assignments. [3]

8. a) The concept of "end group interchange" was used by Fischer in distinguishing the configurational structure of D-glucose and D-mannose. Elucidate. [2]

b) Justify or criticize: [1.5×2]

i) $^4C_1$ conformation of D-glucose is more stable than its $^1C_4$ conformation where as $^1C_4$ conformation of L-galactose is more stable than $^4C_1$ conformation

ii) Formation of D-glucononitrile from D-arabinose is a kinetically controlled reaction.

9. a) Write one chemical reaction of a sugar molecule of your choice with following reagents separately : [1]

i) Triphenylmethyl chloride

ii) N-methylphenylhydrazine

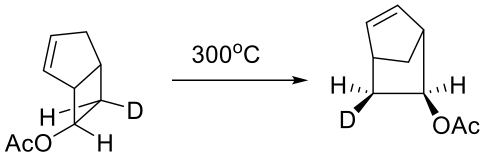
b) Justify or criticize: [2×2]

i) Mutarotation of D-glucose is a case of first order asymmetric transformation which is not true for mutarotation of D-ribose.

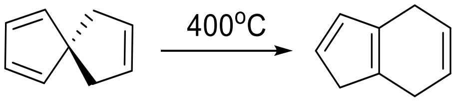
ii) The genetic information content comes down simply to two sets of hydrogen bonds.

10. a) Explain the products formation for the following reactions [2×2]

i)



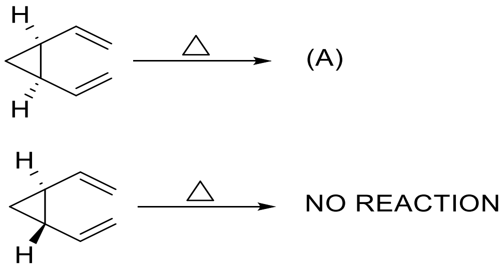
ii)



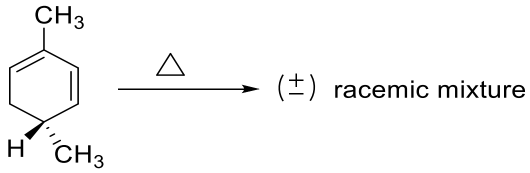
b) Give one suitable use for the following reagents : [1]

i) TBAF ii) TMSCN

11. a) Explain the following observation and also predict the structure for the compound (A). [2]



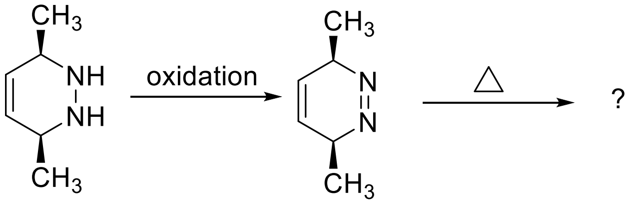
b) Explain the following observation and also predict the structure for the products. [2]

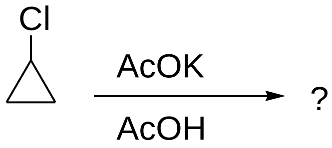


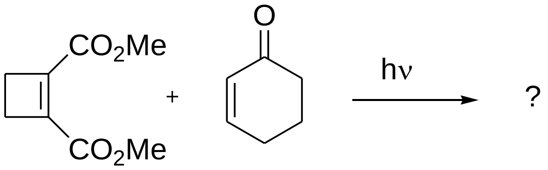
c) Give a suitable comparison between allyl silicon and allyl magnesium reagents. [1]

12. a) Predict the products for the following reactions (no mechanism needed): [1×5]

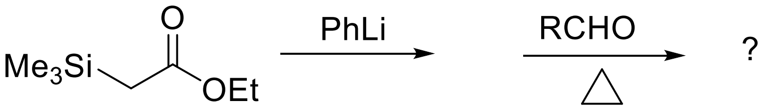
i)



ii) 

iii) 

iv) Trans-3,4-dimethylcyclohexadiene $\xrightarrow{\Delta}$?

v) 

Group – C (Inorganic Chemistry) [5×5]

13\. a) VO, MnO and NiO have Oh-coordination of the metal ion in a rock salt structure. Arrange them in the order of increasing lattice energy value. Explain your arrangement. [2]

b) The observed magnetic moments of Oh-complexes of Mn^{3+}, Fe^{3+} and Co^{3+} are 4.95, 6.6 and 0.00 Bohr Magneton, respectively. Derive the correct electron configuration of Mn^{3+}, Fe^{3+} and Co^{3+}. [3]

14\. a) Arrange Cr^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} with the increase of $\Delta H_{\text{hydration}}$ (magnitude only) with justification. [2]

b) Give the change of the required energy graphically for the gas phase conversion of $M^{2+}(g) \rightarrow M^{3+}(g)$. (Where M stands for first row d-block metal) with justification. [3]

15\. a) E^0 for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} - Why? [3]

b) M-M multiple bond strength increases in their compounds from Cr→ Mo→ W. Why? [2]

16\. a) Calculate the multiplet width between ground and first excited states of a $4f^x$ species of ground term $^5I_8$ (given: single-electron spin-orbit coupling constant ($\xi = 2080\ cm^{-1}$) and hence evaluate the value of magnetic moment and also the value of x. [3]

b) Gd(III) shows magnetic moment equivalent to the number of unpaired electrons – why? [2]

17\. a) The magnetic moment of an An(III) species is lower than the corresponding Ln(III) species - Justify the statement. [2]

b) β-diketonate complexes of Eu(III) can be used as NMR shift reagent. Explain the working principle. [3]

18\. a) Outline the physico-chemical principle based on which lanthanides can be separated by the ion-exchange method. [3]

b) Actinides show multiple oxidation states in their chemistry - why? [2]

Group – D (Analytical Chemistry) [5×5]

19. Commercially EDTA is available as Na_2H_2EDTA (Na_2H_2Y), comment. During complexometric estimation of Ca using EBT as indicator small amount of Mg-salt should be added with EDTA solution, explain with reason; give all the chemical reactions involved. [2+3]

20. For the estimation of Cu in presence of Fe, using $K_2Cr_2O_7$, orthophosphoric acid (H_3PO_4) is not sufficient as masking agent, comment. How can you estimate Cu in presence of Fe titrimetricaly using $K_2Cr_2O_7$? What are the common errors in iodimetric titration? [3+2]

21. a) For the dissolution of brass nitric acid is used but for dissolution of dolomite simply HCl is used, explain with reason, give all the chemical reaction involve. [3]

    b) Comment on the pH dependent of metal ion indicator in complexomertic titration. [2]

22. A chromatogram of a mixture of species A, B, C and D provided the following data.

	Retention time (min.)	Width of peak base (W) (min.)
Nonretained	3.1	
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

If the length of the column packing is 24.7 cm, determine

i) The length of column necessary to separate B and C with a resolution of 1.5.

ii) The time required to separate B and C on the column with a resolution of 1.5. [2.5+2.5]

23. a) Analysis of a sample of iron ore gives the following percentage value of iron content: 7.08, 7.12, 7.21, 7.09, 7.16 and 7.14. Calculate the mean, standard deviation and coefficient of variation for the values. [3]

    b) R_f values of three amino acids A_1, A_2 and A_3 are 0.14, 0.36 and 0.65 respectively. Which one of these amino acids in their TLC separation will occur on the top and which one at the bottom. Provide explanation. [2]

24. a) How do you separate chloride and bromide using ion exchange chromatography? Can cations be separated on an anion exchanger? Provide explanation. [2+1]

    b) In a volumetric determination of an analyte ‘A’, the data obtained and their standard deviations are as follows

	Mean reading	Standard deviation
Initial burette reading	0.19 mL	0.02 mL
Final burette reading	9.26 mL	0.03 mL
Sample mass	45.0 mg	0.2 mg

From the data, find the coefficient of variation of the final result for the % A that is obtained by using the equation that follows (assuming there is no uncertainty in the equivalent mass). [2]

$$\%A = \frac{(titrant\ volume)\times(equivalent\ mas)}{sample\ mass}\times 100\%$$

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