

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, SEPTEMBER 2020

SECOND YEAR (BATCH 2018-21)

CHEMISTRY (Honours)

Date : 26/09/2020

Time : 11.00 am – 3.00 pm

Paper : IV

Full Marks : 50

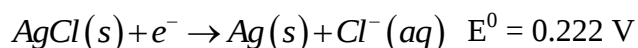
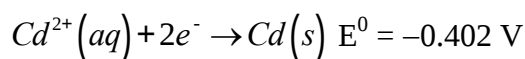
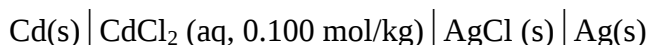
[Attempt all the Groups in the same Answer book]

Group –A (Physical)

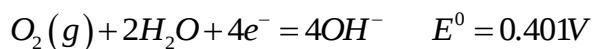
[Attempt any three questions]

[3×6]

1. a) The EMF of the cell $\text{Bi} | \text{Bi}_2\text{S}_3(\text{s}) | \text{Bi}_2\text{S}_3(\text{aq}) | \text{Bi}$ is 0.96 V at 25°C. Calculate (a) the solubility product of Bi_2S_3 and (b) its solubility at 25°C. (Mol Wt of $\text{Bi}_2\text{S}_3 = 514 \text{ g/mol}$) [3]
- b) The mean ionic activity coefficient of CdCl_2 in a 0.100 mol/kg aqueous CdCl_2 solution at 25°C and 1 bar as $\gamma_{\pm} = 0.228$. Find E° and E at 25°C and 1 bar for the cell [3]



2. a) Consider the couple $\text{O} + e^- = \text{R}$ with all of the oxidized and reduced species at unit activity. What must be the value of E° of the couple if the oxidant is to liberate oxygen at 1 atm by the half-cell reaction,



i) from a basic solution, $a_{\text{OH}^-} = 1$?

ii) from an acid solution, $a_{\text{H}^+} = 1$?

iii) Is oxygen a better oxidizing agent in acid or in basic solution? [3×1]

- b) The specific conductance of a saturated solution of BaSO_4 is $3.48 \times 10^{-6} \text{ S/cm}$ and that of pure water is $5 \times 10^{-7} \text{ S/cm}$. The ionic conductance values of Ba^{2+} and SO_4^{2-} ions are 127.26 and $160.04 \text{ S cm}^2/\text{mol}$. Calculate the solubility product of BaSO_4 . [3]
3. a) Specific conductance, equivalent conductance, equivalent conductance at infinite dilution: mention how each of these quantities depend on concentration? [3]
- b) The equivalent conductance of LiCl at infinite dilution is $115.03 \times 10^{-4} \text{ S m}^2/\text{mol}$. The cationic transport number is 0.336. Calculate the mobility of the cation and its velocity if the applied potential difference across two electrodes, 0.4 cm apart, is 6.0 volt. [3]
4. a) An H-like orbital is given below –

$$\psi = A \left(\frac{z}{a} \right)^{5/2} \left(6 - \frac{zr}{a} \right) r e^{-zr/3a} \cos\theta$$

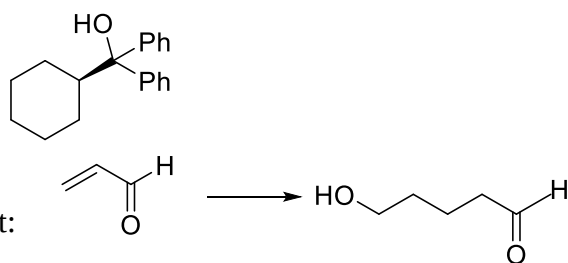
where A is the normalization constant, others are carrying the usual meaning. Determine n, l, m_l for the function, by simple inspection. Which orbital does it represent? [2]

- b) Present the radial equation of H atom ($z = 1$) as an eigenvalue equation in a.u. and verify that $R_{20}(r) = \frac{1}{2\sqrt{2}}(2 - r)e^{-r/2}$ is a normalized eigenfunction. [1+2]
- c) Calculate the orbital angular momentum value of 3d electron and show its orientation. [1]
5. a) Verify that $\langle 1/r \rangle$ for 1s electron of H-like atom is $1/a_0$. Given that $\psi_{1s} = \frac{e^{-r/a_0}}{\sqrt{\pi}a_0^{3/2}}$. [2]
- b) Give a qualitative plot of radial functions for 2s and 2p orbitals of H-like atom, in same graph. Also comment on the appearance of node in these orbitals. [2]
- c) Show that, the degeneracy for nth energy level of H atom is n^2 . [2]

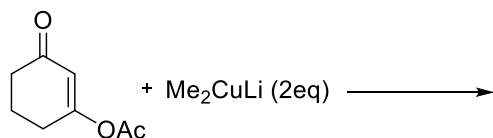
Group – B (Organic)
[Attempt any four questions]

[4×4]

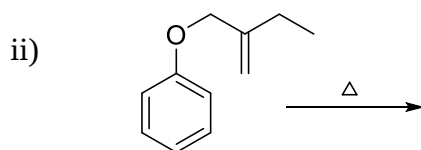
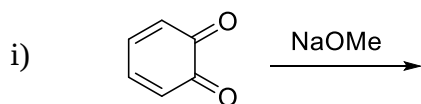
6. a) Give retrosynthetic analysis and an efficient synthesis of the molecule below: [2]



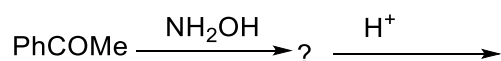
- b) Convert: [2]
7. a) Predict the product for the following reaction: [2]



- b) “Diazomethane is an excellent reagent for ring expansion reaction” -- Justify the statement giving example. [1]
- c) “Phthalimide is an excellent choice as starting material for the synthesis of primary amine”- justify. [1]
8. Predict the product(s) formation and also explain the mechanism: [2×2]

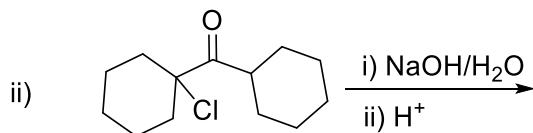
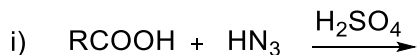


9. a) Predict the product formation and also explain the mechanism: [2]



b) Justify or criticize: “Hoffmann bromamide degradation is an intramolecular rearrangement”. [2]

10. a) Predict the product formation and also explain the mechanism: [2×2]



Group – C (Inorganic)

[Attempt any four questions]

[4×4]

11. a) Write down the structure of “Borax” mentioning hybrid orbitals used by the boron centres. [2]

b) Aqueous borax solution has buffering property – why? [1]

c) Complete the following reaction: $\text{Borax} + \text{CaF}_2 + \text{H}_2\text{SO}_4$ (anhydrous) $\rightarrow$ [1]

12. a) Using MOT, give B-H-B bonding in B_2H_6 . [2]

b) Give the similarity and dissimilarity of anhydrous BCl_3 and anhydrous AlCl_3 at their gas phase in the light of (i) Lewis acidity, (ii) structure. [2]

13. a) Layered $(\text{BN})_x$ though has graphite like structure but insulator-why? [2]

b) Trisilyl amine and trimethyl amine reacts differently with HCl -why? Write the reaction products in each case. [2]

14. What are silicones? Mention the different precursor units for silicon synthesis. How are they prepared? [1+1+2]

15. What are pseudo halogens? Why they are so called? What are the basic differences between halogens and pseudo halogens? [1+2+1]

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