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Birla Institute of Technology & Science, Pilani, Rajasthan 333031
Second Semester 2022-2023

Course Number: CHEM F341

Course Title: Chemical Experimentation Lab II

Test syllabus: Cycle I experiments

Marks: 24

Time: 30 min

Experiment 1 & 2: Computation of electronic structure of molecules - I and II (8M)

Q1. If $A_{\mu,\nu} = \sum_j n_j (2c_{\mu,j}c_{\nu,j}S_{\mu,\nu})$, where, μ and ν are AO indices, j is MO index, then the quantity $A_{\mu,\nu}$ represents [2]

- (a) overlap matrix element (b) charge-density bond-order matrix element
(c) AO-MO coefficient matrix element (d) Overlap population between an AO-pair

Q2. In the Z-matrix for specifying internal coordinates of benzaldehyde, the number of bond angles and plane angles required for obtaining unambiguous geometry are, respectively _____ and _____. [2]

Q3. The harmonic frequencies of normal modes of vibrations of a molecule are directly proportional to [2]

- (a) energy gradient (b) eigen-values of hessian matrix
(c) square root of components of gradient (d) square-root of hessian matrix eigen-values

Q4. The nuclear repulsion energies of a diatomic molecule in its lowest singlet and lowest triplet states are represented by $V_{NN}(S)$ and $V_{NN}(T)$, respectively. If $V_{NN}(T) > V_{NN}(S)$, then which of the following statements is true? [2]

- (a) The ground state must be singlet (b) The triplet state must be a transition state
(c) The bond is shorter in the triplet (d) The singlet has larger ZPE

Experiment 3: Linkage Isomerism (4M)

Q1. $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ are linkage isomers. One of the isomers is thermodynamically controlled product (TCP) while the other one is kinetically controlled product (KCP). Which of the following statements correctly explains these two isomers. [1]

- (a) $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ is KCP as it has more negative CFSE leading to more stability compared to $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
(b) $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ is TCP as the attack of NO_2 via N centre occurs faster compared to the attack of NO_2 via O centre to form $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
(c) $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ is KCP as the attack of NO_2 via O centre occurs faster compared to the attack of NO_2 via N centre to form $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
(d) $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ is KCP as it has more negative CFSE leading to more stability compared to $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$

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Q2. Check the following reactions (reactions are not balanced) and choose the correct option [1]



- (a) [P1] = $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$ and Primary valency of [P2] is 2
(b) [P1] = $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{3+}$ and Primary valency of [P2] is 3
(c) [P1] = $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{3+}$ and Primary valency of [P2] is 2
(d) [P1] = $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$ and Primary valency of [P2] is 3

Q3. $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ shows two IR peaks at 1460 and 1055 cm^{-1} related to -ONO group and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ shows two IR peaks at 1426 and 1365 cm^{-1} related to -NO₂ group. The assignments of the peaks are [1]

- (a) 1460 cm^{-1} : Symmetric str; 1055 cm^{-1} : Asymmetric. str; 1426 cm^{-1} : N=O; 1365 cm^{-1} : N-O
(b) 1460 cm^{-1} : Asymmetric str; 1055 cm^{-1} : Symmetric. str; 1426 cm^{-1} : N=O; 1365 cm^{-1} : N-O
(c) 1460 cm^{-1} : N=O; 1055 cm^{-1} : N-O; 1426 cm^{-1} : N-O; 1365 cm^{-1} : N=O
(d) 1460 cm^{-1} : N=O, 1055 cm^{-1} : N-O; 1426 cm^{-1} : N=O, 1365 cm^{-1} : N-O

Q4. Why did you observe the shift in peak position in the region of (400 – 500) nm of UV-Vis spectrum of the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ from that of the $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ complex. [1]

Answer:

Experiment 4: Synthesis of Au Nanoparticles and application in Catalysis (4M)

Q1. In a typical synthesis for 8 nm gold colloid, an aliquot of HAuCl_4 (1.25 ml of 10^{-2} M) was heated to boiling in 50 ml water and then 2.0 mL of LiAlH_4 was added instead of trisodium citrate and wait for ~8 minutes. No other chemicals were added. The solution was set aside to cool down to room temperature. Which of the following statement is correct regarding the formation of Au nanoparticles? [1]

- (a) Au nanoparticles will form but precipitated after some time
(b) Au nanoparticles will form and remain stable
(c) Au nanoparticles won't form as LiAlH_4 is a mild reducing agent
(d) LiAlH_4 will form a complex with HAuCl_4 and difficult to reduce HAuCl_4 .

Q2. To study the size effect on the process of the metallic gold particles in the nanometer size regime, it is important to have sets of nanoparticles within the range of 1-100 nm with a tight size distribution. The well-documented Frens' method was used to obtain

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monodispersed gold colloids over a wide size range keeping unchanged the amount of HAuCl_4 . From the table it is clear that higher amount of trisodium citrate lowers the particle size. This is due to,..... [1]

(a) Higher amount of trisodium citrate covers the reduced Au particles more and it is impossible for other reduced particles to come and combine with already formed cluster, therefore lowers the particle size.

(b) Higher amount of trisodium citrate covers the HAuCl_4 ions more and it is impossible for trisodium citrate to reduce further, therefore lowers the particle size.

(c) Trisodium citrate can only reduce HAuCl_4 to Au nanoparticles but unable to protect the Au particles further, therefore lowers the particle size.

(d) Higher amount of trisodium citrate reduce the entire amount of HAuCl_4 at a time and lowers the particle size.

Q3. In a chemical reaction, the rate constant is found to be 0.25 min^{-1} . What is the half-life of this reaction? [1]

(a) 0.69 min

(b) 1.54 min

(c) 2.77 min

(d) 3.75 min

Q4. The rate of the reaction from p-nitrophenol to p-aminophenol is decreasing with enhancing size of Au nanoparticles. What could be the reason behind this? Write in two sentences only. [1]

Answer:

Experiment 5: Determination of critical micellization concentration (4M)

Q1. Choose the correct option: [1]

Statement: The fluorescence intensity of the probe varies with gradual increase in the concentration of the surfactant into the aqueous medium.

(a) The slope of the line obtained after cmc is reduced than the slope of the line obtained before cmc because the probe is surrounded with hydrophilic environment

(b) The slope of the line obtained after cmc is reduced than the slope of the line obtained before cmc because the probe is surrounded with hydrophobic environment

(c) The slope of the line obtained after cmc is increased than the slope of the line obtained before cmc because the probe is surrounded with hydrophilic environment

(d) The slope of the line obtained after cmc is increased than the slope of the line obtained before cmc because the probe is surrounded with hydrophobic environment

(cmc = critical micelle concentration)

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Q2. Choose the correct option: [1]

(a) Sodium dodecyl sulphate was excited at 378 nm, then it efficiently transfers the energy to *p*-dimethylaminocinnamaldehyde, hence the emission was observed at 478 nm from *p*-dimethylaminocinnamaldehyde

(b) *p*-Dimethylaminocinnamaldehyde was excited at 378 nm and the emission was observed at 478 nm from *p*-dimethylaminocinnamaldehyde

(c) *p*-Dimethylaminocinnamaldehyde was excited at 378 nm, then it efficiently transfer the energy to sodium dodecyl sulphate, hence the emission was observed at 478 nm from sodium dodecyl sulphate

(d) Sodium dodecyl sulphate was excited at 378 nm and the emission was observed at 478 nm from sodium dodecyl sulphate



Q3. In a conductivity cell, two platinum electrodes, each having a cross-sectional area of 4.2 cm^2 , is separated by a distance of 1.4 cm. Using this cell, conductance of 0.5 N electrolyte was measured as 0.066 S. [1+1]

I. Specific conductance of the electrolytic solution is Sm^{-1} .

II. In the above cell, when 0.025 M sodium dodecyl sulphate (SDS) was added, the specific conductance changed to 5.235 Sm^{-1} . The molar conductance of sodium dodecyl sulphate is $\text{Sm}^2\text{mol}^{-1}$ (assume that there is no change in molar concentration of SDS).

Experiment 6: Illustrating the Nernst equation (4M)

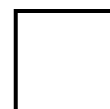
Q1. Cyclic voltammetry is a.....technique andvs..... is plotted [1]

(a) Destructive, Potential vs. Concentration

(b) Non-destructive, Potential vs. time

(c) Destructive, Current vs. time

(d) Non-destructive, Current vs. Potential



Q2. For the electrochemical study of 'Validation of Nernst equation' as a counter electrode we have used.....electrode. [1]

Q3. Write the cell reaction of the following cell: Pt: $\text{K}_4[\text{Fe}(\text{CN})_6]$ (aq.) / $\text{K}_3[\text{Fe}(\text{CN})_6]$ (aq.) // Fe^{2+} / Fe. Find out the cell potential and comment on the spontaneity of the reaction. Given, $E^0_{\text{Fe}^{2+}/\text{Fe}} = -0.447 \text{ V}$; $E^0_{\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]} = 0.37 \text{ V}$ at $T = 28 \text{ }^\circ\text{C}$ [1+1]

Answer:

*****END*****