

Five Year Integrated M.Sc. Examination 2023

Semester - V

Course: CH-3-5-1

(Chemistry)

Time: Four Hours

Full Marks: 80

Questions are of value as indicated in the margin

Group-A

1. Answer **any ten** questions:

10 × 2 = 20

- (a) What will be geometry of the following molecules?
(i) I_3^- and (ii) ICl_2^-
- (b) Calculate the bond order per H-H link of H_8 molecule.
- (c) Comment on the stability order of H_3 and H_3^+ .
- (d) What do you mean by Terminal Atom Symmetry Orbitals?
- (e) Show the splitting pattern of d -orbitals in octahedral and tetrahedral crystal field.
- (f) Find out the octahedral site stabilization energy (OSSE) for a d^3 system.
- (g) Comment on the magnetic property of $[Fe(NCS)_2(phen)_2]$.
- (h) Color of $trans-[Co(en)_2F_2]^+$ is less intense than the *cis*-isomer. Explain.
- (i) Cyclopropylmethyl cations are even more stable than the benzylic type. Explain.
- (j) Although phenyl group is bulkier than methyl group, $PhCH_2Cl$ and CH_3CH_2Cl undergo S_N2 reaction at almost same rate. Why?
- (k) Iodide is both an excellent nucleophile and leaving group, why alkoxides are good nucleophiles but lousy leaving groups.
- (l) Explain whether the reaction of 1-chloropropane with ammonia will be faster in 20% MeOH-80% water or in 40% MeOH-60% water?

Group-B

Answer **any four** questions

2. (a) Show the Walsh diagram of water (H_2O) molecule and give reasons for change of energy of molecular orbitals with the variation of bond angle. 2+3
3. Sketch the involved group orbitals (TASO) of a triatomic hydrogen species and show the involved MO diagram. 3+2
4. Draw the involved sigma type molecular orbitals of BH_2 molecule by considering participation of H-group orbitals and show their energy order. 4+1

5. Draw the probable geometry of sulphur tetrafluoride and select the most stable geometry according to VSEPR theory. 2+3
6. State Bent's rules and justify the geometry of chlorine trifluoride according to it. 2+3

Group-C

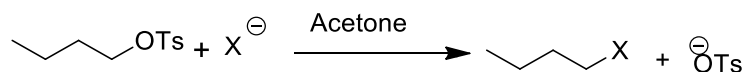
Answer *any four* questions

7. (a) Discuss about the tetragonal Jahn Teller distortion observed in Cu^{2+} system. 2
(b) What do you understand by Laporte and spin forbidden transition? What are the situations when Laporte forbidden transitions become possible? 2+1
8. (a) Write a short note on nephelauxetic effect. 2
(b) Explain the origin of color in HgI_2 . Why HgCl_2 is colorless? 2+1
9. (a) Define diamagnetic and paramagnetic substances and comment on their magnetic susceptibility. 2
(b) Determine the crystal field stabilization energy, number of unpaired electrons and magnetic moment (spin-only) of the metal ion in $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{FeF}_6]^{3-}$. 3
10. (a) Find out the total number of microstates for a d^2 system. Find out the term symbols of the ground state and first excited state for this system. 3
(b) Draw the Orgel diagram for the d^2 electronic state and show the possible transitions. 2
11. (a) Establish what type of spinel is Fe_3O_4 . 2
(b) What do you understand by a magnetically dilute substance? Explain the magnetic behavior of substances that are not magnetically dilute. 3

Group-D

Answer *any four* questions

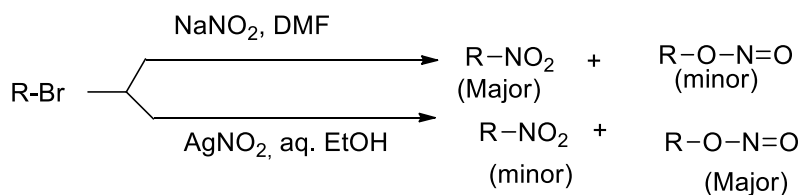
12. a) Provide an explanation for the observation that nucleophilic substitution of 4-bromo-2,6-dimethylnitrobenzene is considerably slower than that of 4-bromonitrobenzene. 2
(b) Account for the following observations: 3



In the reactions,

The order of nucleophilicity for the various halides is $\text{I}^- > \text{Br}^- > \text{Cl}^-$, when LiX is used, but the order is $\text{Cl}^- > \text{Br}^- > \text{I}^-$ when $\text{Bu}_4\text{N}^+\text{X}^-$ is used.

13. (a) Let us consider the following substitution reaction and explain the following observation: 2.5



(b) Convert: (S)-2-pentanol to (R)-2-pentanol.

2.5

14. (a) α -Halo carbonyl compounds are excellent substrates for S_N2 reactions but react very slowly in S_N1 conditions. Why?

2.0

(b) Provide a plausible mechanism for the following transformation:

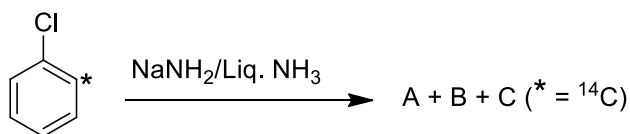
3.0



Is there a special reason to use DMF as the solvent here? Account for the fact that if a methyl ester is taken instead of the ethyl ester the rate of the reaction increases about 10 times.

15. (a) Identify the products and explain their formation.

2.5



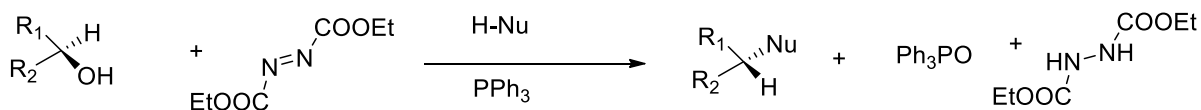
(b) Explain the following relative rates that were observed during bromination of the alkane under photochemical condition:

2.5

Me-H	MeCH ₂ -H	Me ₂ CH-H	Me ₃ C-H	PhCH ₂ -H
0.0007	1	220	19,400	64,000

16. (a) Explain the following reaction mechanistically:

2.0



(b) Explain the observation:

3.0

