

Ans

INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR  
DEPARTMENT OF CHEMISTRY

Autumn 2015 End-Semester Examination  
Subject No./Name: CY11001 / Chemistry

No. of Students: 660  
Full Marks: 50 + 50 Time: 3h

(Please read all the instructions given below before answering the questions)  
(This question paper contains 5 pages)

1. This Question Paper has **TWO** parts (PART-A and PART-B). Make sure that you have both **PART-A** and **PART-B** of the Question Paper.
2. Use **SEPARATE ANSWER SCRIPTS** for PART-A and PART-B.
3. **WRITE** your NAME, ROLL NO. and SECTION No. **IN BOTH THE ANSWER SCRIPTS**.
4. **SUBMIT THE ANSWER SCRIPTS** for PART-A and PART-B **SEPARATELY** to the invigilator on completion of the Examination.
5. **WRITE ANSWERS SERIALY; OTHERWISE THEY WOULD NOT BE CHECKED.**

**Part A: Inorganic Chemistry**

[Atomic Nos: Mn: 25, Fe: 26, Co: 27, Rh: 45, V: 23, Cr: 24, Ni: 28. Velocity of light:  $2.998 \times 10^8$  m/sec; Mass of electron:  $9.1095 \times 10^{-28}$  g; Gas constant: 8.314 J/mol/K; Farady's constant:  $9.648 \times 10^3$  emu; Joule's constant: 4.18 Joule/cal; Avogadro constant:  $6.0021 \times 10^{23}$  mole<sup>-1</sup>; Planck's constant:  $6.626 \times 10^{-34}$  J s; 1 eV =  $1.602 \times 10^{-19}$  J = 96.485 KJ/mol]

Answer all the questions:

1. (a) The work function of sodium is 2.5 eV. Predict whether the photon with wavelength of 6800 Å is suitable to eject photoelectron or not? 2  
(b) Write the Hamiltonian and Schrödinger equation for the H<sub>2</sub><sup>+</sup> species. 3
2. (a) Draw the MO diagram of B<sub>2</sub> and show reason(s) for showing paramagnetism. Label the molecular orbitals with σ, π, g and u notations. Identify the molecular orbitals (if any) which undergo orbital mixing. 4  
(b) Between O<sub>2</sub> and O<sub>2</sub><sup>-</sup>, which one has longer bond length and why? 1
3. (a) Why does metallic copper show good electrical conductivity? 2  
(b) What is π-acid ligand? Give an example. 1  
(c) How does one π-acid ligand stabilize metal ions with low oxidation state forming stable organometallic complexes? Explain by showing orbital overlap responsible for forming the corresponding metal-ligand bond with proper labelling of the orbitals. 2
4. (a) Construct the Frost diagram of Mn from the following Latimer diagram (acidic medium). Show the required calculation and diagram with properly labelling of the axes. 4  

$$\text{MnO}_4^- \xrightarrow{0.90} \text{HMnO}_4^- \xrightarrow{1.28} \text{H}_3\text{MnO}_4 \xrightarrow{2.9} \text{MnO}_2 \xrightarrow{0.95} \text{Mn}^{3+} \xrightarrow{1.5} \text{Mn}^{2+} \xrightarrow{-1.18} \text{Mn}$$
  
(b) From the Frost diagram, explain why Mn<sup>3+</sup> is unstable in acidic solution. 1
5. The spin only magnetic moment values of two complexes, [Fe(L<sub>A</sub>)<sub>6</sub>]<sup>3-</sup> and [Fe(L<sub>B</sub>)<sub>6</sub>]<sup>3-</sup>, are 1.73 B.M and 5.92 B.M., respectively. L<sub>A</sub> and L<sub>B</sub> are mono-anionic ligands.  
(a) Between L<sub>A</sub> and L<sub>B</sub>, which one is a strong-field ligand? 1  
(b) Show the splitting of d-orbitals and electron distribution to account for the magnetic moment of each complex. 2

- (c) Calculate the CFSE values for both the complexes. 2
6. (a) Between weak field  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$  octahedral complexes, in which case do you expect strong Jahn-Teller distortion and why? 2
- (b) Write down the expected product if excess  $\text{CN}^-$  is treated with an aqueous solution of  $\text{Ni}^{2+}$ . 3  
Show the splitting of d-orbitals with electron distribution for the resulting complex.
7. (a) Solutions of the complexes  $[\text{Co}(\text{NH}_3)_6]^{2+}$ ,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{CoCl}_4]^{2-}$  are all colored. One is blue, another is yellow and third one is pink. Considering the spectrochemical series of ligands and relative magnitude of  $\Delta_T$  and  $\Delta_O$ , assign color for each of the complexes. 3
- (b) Between  $\text{V}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$ , which one can show oxidizing power and why? 2
8. (a) The  $\log \beta$  for  $[\text{Cd}(\text{en})_2]^{2+}$  (en = ethylenediamine) formation is greater than that of  $[\text{Cd}(\text{MeNH}_2)_4]^{2+}$  although  $\Delta H$  values for both the reactions are very similar. Determine the thermodynamic parameters (at  $T = 298 \text{ K}$ ) responsible for the following reactions, and account for the marked difference in  $\log \beta$ .
- $$\begin{array}{c}
 [\text{Cd}(\text{en})_2]^{2+} \xleftarrow[2 \text{ "en"}]{\log \beta = 10.6; \Delta H = -56 \text{ kJmol}^{-1}} \text{Aqueous Cd}^{2+} \xrightarrow[4 \text{ MeNH}_2]{\log \beta = 6.5; \Delta H = -57 \text{ kJmol}^{-1}} [\text{Cd}(\text{MeNH}_2)_4]^{2+}
 \end{array}$$
- (b)  $\text{EDTA}^{4-}$  (ethylenediaminetetraacetate) is used to remove heavy toxic metal cations such as  $\text{Pb}^{2+}$  from human body through *chelation therapy*. Explain the mode of action of  $\text{EDTA}^{4-}$  and how the  $\text{Pb}^{2+}$  is eliminated from body. 2
9. (a) What is the active catalyst used in Monsanto acetic acid process? 1
- (b) Draw the structures of the missing products of this reaction. Mention the type of reaction and change in oxidation state of "Rh". 2
- $$\begin{array}{c}
 \begin{array}{c} \text{Me} \\ | \\ \text{C}=\text{O} \\ | \\ \text{Rh} \\ | \\ \text{CO} \end{array} \xrightarrow{\text{CO}} \begin{array}{c} \text{Me} \\ | \\ \text{C}=\text{O} \\ | \\ \text{Rh} \\ | \\ \text{CO} \end{array} \longrightarrow ?
 \end{array}$$
- (c) Write down the expected organometallic compound in the following reaction. Mention the type of reaction and give reason why does the reaction undergo? 2
- $$\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{Rh} \\ | \\ \text{H}_3\text{C} \end{array} \begin{array}{c} \text{CO} \\ | \\ \text{CO} \end{array} \xrightarrow{\text{CH}_3\text{CH}_2\text{I}} ?$$
10. (a) Show the active site of Hemoglobin mentioning the oxidation state of the metal centre, geometry around the metal centre, and *heme* group. 4
- (b) Why oxy-hemocyanin is blue colored but deoxy-hemocyanin is colorless? 1

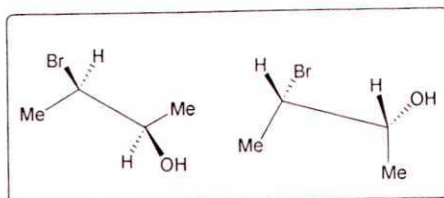
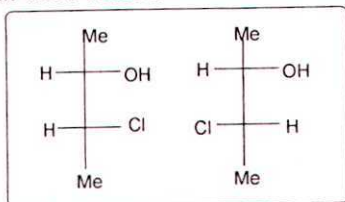
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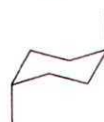
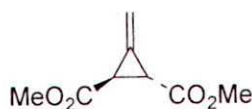
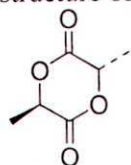
## Part B: Organic Chemistry

(Answer all questions in a separate answer sheet with your name, roll number and section)

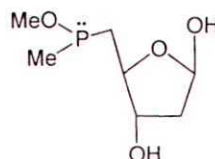
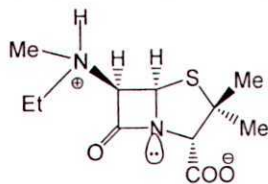
1. a) Indicate the relationship between the compounds of the following pairs as identical or enantiomers or diastereomers. Also indicate configurations of the stereogenic centers as 'R' or 'S' showing the priority sequence at each centre. [2+2 = 4]



- b) Draw the stereostructure of a diastereoisomer for each of the following and label them as chiral/achiral. [1+1+1 = 3]

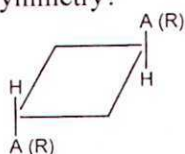
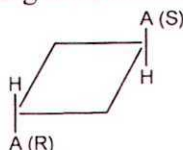


- c) How many stereogenic center(s) is(are) present in each of the following molecules? Indicate them in the structures. [1+1=2]



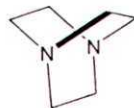
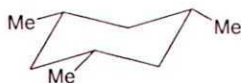
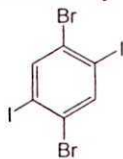
OR

- Which of the following molecules have center of symmetry? [1+1=2]



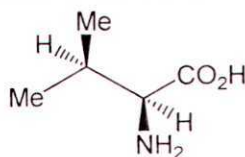
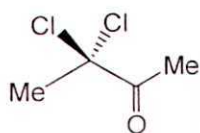
A is a substituent with stereogenic centre in R or S configuration

- d) How many planes of symmetry does each of the following molecules possess? [3]

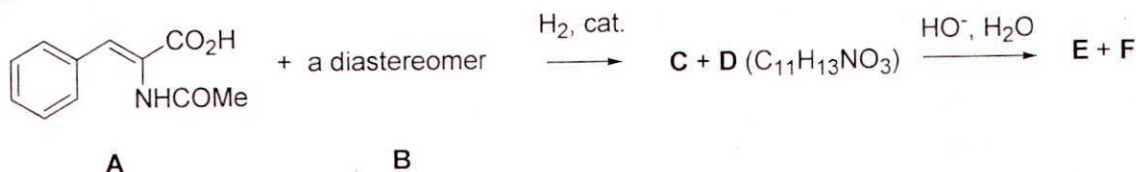


OR

- Assign proR/proS configurations to the ligands as attached to the pro-stereogenic center. Also determine their topicity (enatio/diastereo). [3]



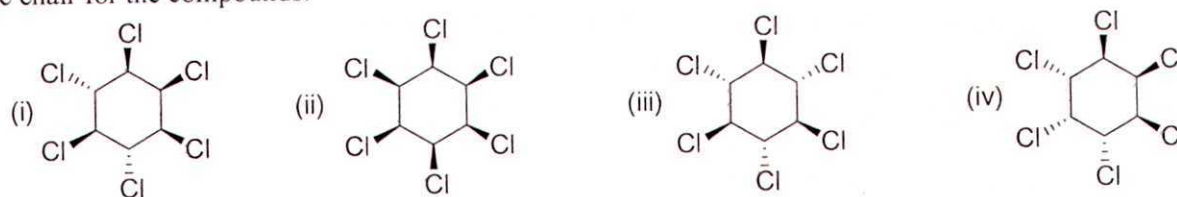
e) A mixture of two diastereoisomeric acids A and B, on catalytic hydrogenation, gives a racemic mixture of C and D ( $C_{11}H_{13}NO_3$ ). The mixture, on alkaline hydrolysis, gives E and F. Write the structures of B, C, D, E and F. Comment on the optical activity of final mixture of products. Also assign E/Z configuration to A and B. [4]



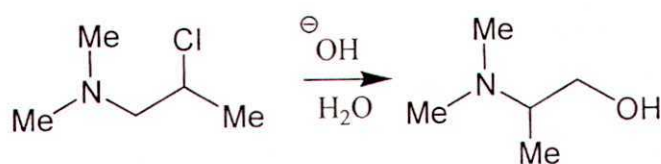
2. Draw all preferred conformations of the stereoisomers of 1,3-dimethylcyclohexane. Calculate their energy difference and comment on their optical activity. [6]

3. (a) Among 1-bromo-3-methylbutane, 2-bromo-3-methylbutane and 2-bromo-2-methylbutane, identify the one i) that undergoes faster  $S_N2$  with NaOMe ii) undergoes faster  $S_N1$  in EtOH; iii) that is optically active and produces an optically active compound when treated with  $NaN_3$  in  $S_N2$  mechanism. [6]

b) Which of the following hexachlorocyclohexanes is the least reactive in an E2 reaction. Explain by writing the chair for the compounds. [4]

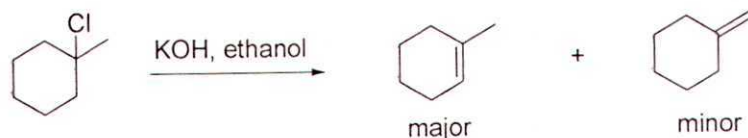


c) Draw a mechanism for the following transformation: [3+1=4]

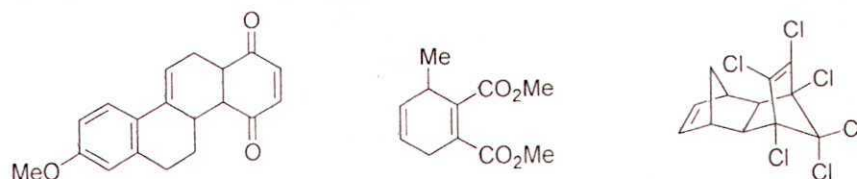


If the absolute configuration of the stereogenic center in the starting material is R, what will be the absolute configuration of the stereogenic center in the product? Give reasons for your answer.

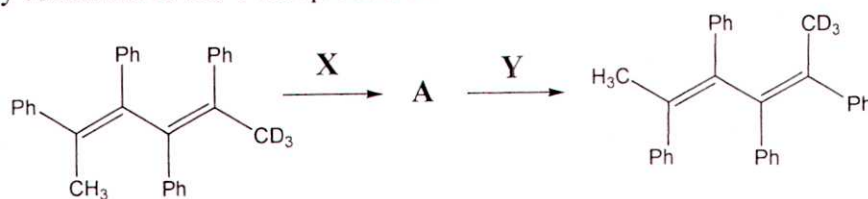
d) For the following E2 elimination reaction, draw the structures of transition states for both products and explain why 1-methylcyclohexene is formed as the major product. [4]



4. (a) Draw the structures of the dienophiles that are needed to synthesize the following compounds by Diels-Alder reactions. [3]

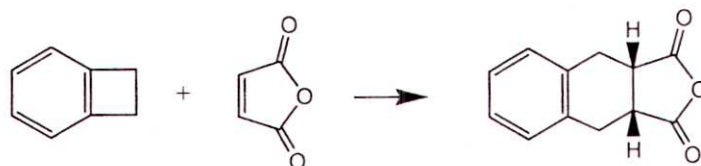


b) Identify conditions X and Y and product A. [4]

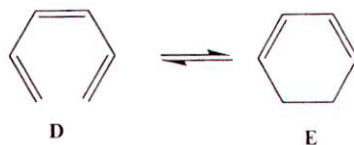


OR

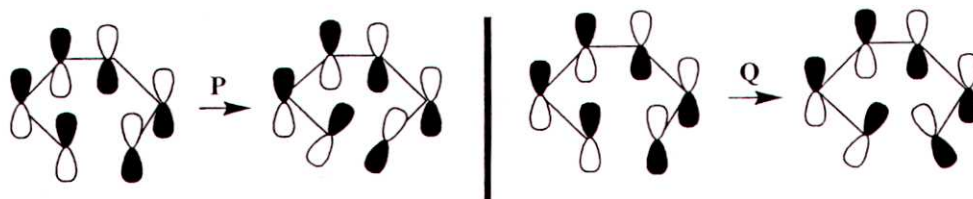
Two sequential separate pericyclic reactions are involved in the following transformation. Identify them and indicate their sequence of occurrence. [4]



c) The following electrocyclization process can be carried out either thermally or photochemically. [3]



One of the  $\pi$ -molecular orbitals for **D** along with their orientation during cyclization processes **P** and **Q** are shown:



Consider the above MO picture and answer the following:

- Which of process **P** or **Q** denotes conrotatory ring closure?
- Which process **P** or **Q** denotes disrotatory ring closure?
- Based on the aromatic transition state theory, find out which process **P** or **Q** is allowed thermally?

.....End of Part B.....

*Handwritten signature and date: 2/11/15*