INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR
DEPARTMENT OF CHEMISTRY

Autumn Examination, 2016 -17 No. of Students: 650
Subject No./Name: CY11001 / Chemistry Full Marks: 50 + 50 Time: 3h

Important instructions are given below and please read before answering the questions:

1. **This Question Paper has TWO parts (PART-A and PART-B) and the paper contains 06 pages.**
2. **SUBMIT THE ANSWER SCRIPTS for PART-A and PART-B SEPARATELY to the invigilator on completion of the Examination.**

Part A: Inorganic Chemistry: *Answer all the questions*

[Given Data: Atomic Nos: N:7, O:8, F:9, Cr:24, Fe:26, Cu:29, Ru:44, Rh:45, Pb:82. Velocity of light: 3.0×10^8 m/sec; Mass of electron: 9.1095×10^{-28} g; Gas constant: 8.314 J/mol/K; Farady's constant: 9.648×10^3 emu; Joule's constant: 4.18 J/cal; Avogadro constant; 6.0231×10^{23} $mole^{-1}$; Planck's constant: 6.626×10^{-34} J s; 1 eV = 1.602×10^{-19} J = 96.485 kJ/mol]

1. (a) How can you increase the kinetic energy of ejected photoelectrons? Mention three flaws of classical mechanics. **[3]**

(b) The work function of a metal is 3.44×10^{-18} J. When it was irradiated by light it ejects electrons with a velocity of 1.03×10^6 m s^{-1}. What could be the wavelength of incident radiation shined on the metal? **[2]**

2. Draw the MO diagram of F_2 with electrons and label the energy levels. **[3+2]**
If a fluorine molecule accepts one electron, what will occur to its bond length in comparison to the parent molecule?

3. (a) "CO" is a π acid ligand, explain the statement using orbital diagram. **[3]**

(b) Why metals possess malleable and ductile properties? **[2]**

4. (a) Calculate the crystal field stabilization energy (CFSE) of $[Fe(CN)_6]^{3-}$ and calculate the spin only mangnetic moment (μ_s) of the complex. **[3]**

(b) Crystal field splitting energy (Δ_O) of two octahedral systems, $[Ru(H_2O)_6]^{2+}$ and $[Ru(H_2O)_6]^{3+}$, are 19800 cm^{-1} and 28600 cm^{-1}, respectively. Discuss the reason for the above difference. **[2]**

5. (a) When aqueous solution of metal (II) salt is reacted with two different reagents, the following coordination compounds (**A** and **B**) are obtained (en= ethylenediamine). **[3]**

$$M^{2+}(aq) + 4NH_3 \rightarrow [M(NH_3)_4]^{2+}(aq);\ \log\beta = 4.31,\ \Delta H = -92\ kJ/mol$$

(A)

$$M^{2+}(aq) + 2en \rightarrow [M(en)_2]^{2+}(aq);\ \log\beta = 20.03,\ \Delta H = -107\ kJ/mol$$

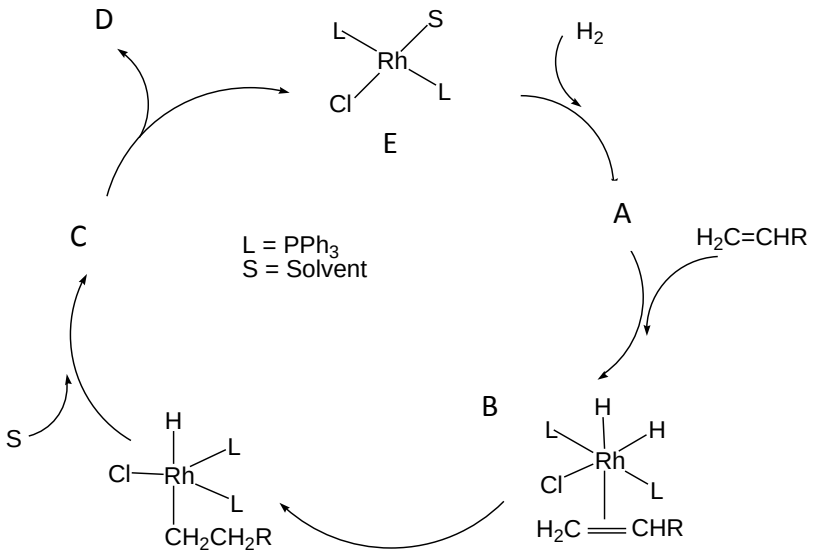
(B)

(i) Calculate the thermodynamic parameters responsible for the above reactions at temperature 298 K.

(ii) Justify the reasons favouring formation of A and B using calculated parameters.

(b) Write the chemical reaction of dimercaprol responsible for the removal of lead or arsenic ions in chelation therapy? **[2]**

6. (a) Identify the missing products with the structures A, C and D; and also count the EAN (effective atomic number) on the compound B. **[4]**



(b) Identify the expected organometallic product for the following reaction: **[1]**

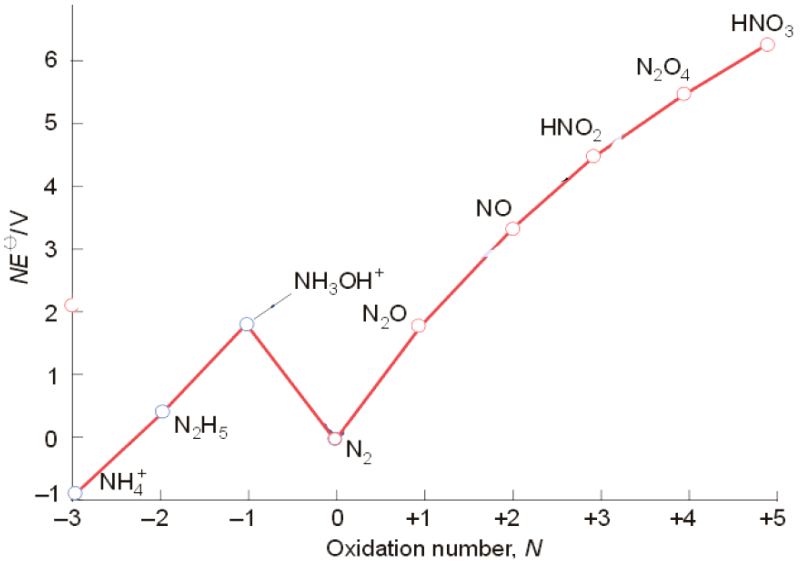
$$[Rh(CO)_2 I_2]^- + MeI \longrightarrow \ ?$$

7. (a) (i) Draw the chemical structure of oxy-haemoglobin. **[3+2]**

(ii) Provide the electronic configuration and spin state of oxy and de-oxy haemoglobin.

(b) Which will undergo Jahn Teller distortion between $[Cu(NH_3)_6]^{2+}$ and $[Cr(NH_3)_6]^{3+}$ complex. Provide the d-orbital splitting pattern with distribution of electrons for both the complexes. **[1+4]**

8. (a) Consider HNO_3 (NE^0 +6.2 V) and NO (NE^0 +3.4V) are reduced to elemental nitrogen separately in acid medium. Determine the stronger oxidant between the two. **[2]**



(b) Latimer diagram for oxygen (in acidic medium) is given below: **[2+5+1]**

$$O_2 \xrightarrow{+0.70\ V} H_2O_2 \xrightarrow{+1.76\ V} H_2O$$

Use the above diagram and answer the following:

(i) Whether it is easy to obtain H_2O from O_2? Explain with a suitable reason.

(ii) Construct the Frost diagram of O_2 from the above Latimer diagram (acidic medium) with properly labelling of the axes along with required calculation and half reactions.

(iii) From the constructed Frost diagram, predict whether peroxide will undergo comproportionation reaction in acidic medium.

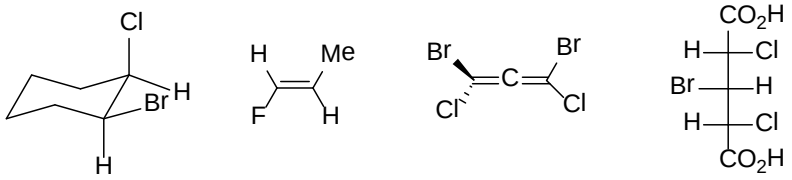
.....End of Part A.....

Part B: Organic Chemistry

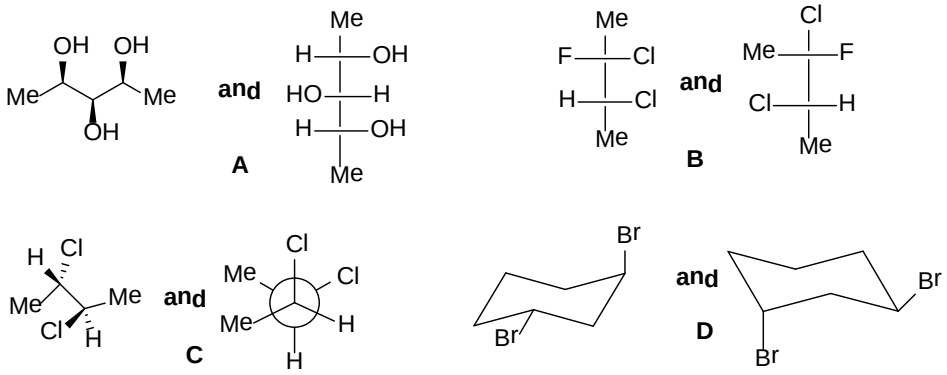
Answer all the questions. **Write in <u>SEPARATE</u> Answer Book.**

1. How many stereogenic center(s) is(are) present in each of the following molecules? **[8]**

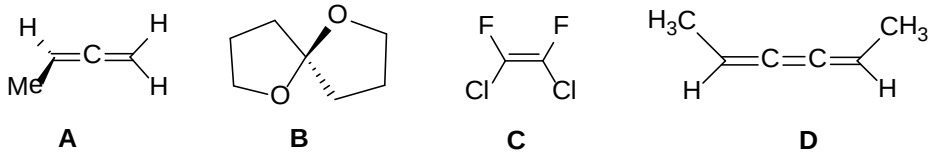
(a) Assign their absolute configurations showing the priority sequence at each centre.



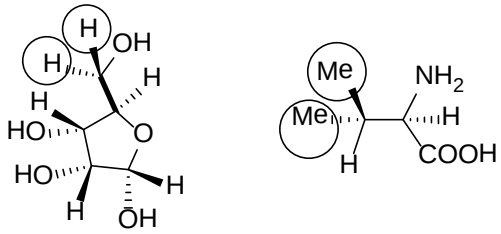
(b) Indicate the relationship between the members of the following pairs (**A**-**D**) of compounds as identical, enantiomers or diastereomers. **[6]**



(c) How many S1 axis (axes) is/are present in the following molecules? **[4]**

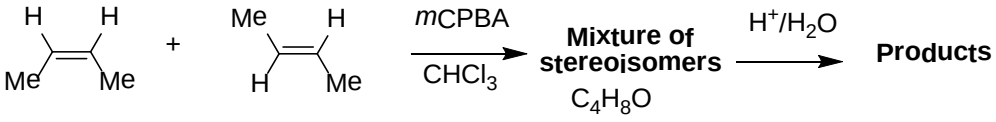


(d) Indicate the relationship between the circled ligands/atoms based on topicity. **[2]**



2. An equimolar mixture of *cis*- and *trans*-2 butene was reacted with *m*CPBA in **[6]**

(a) chloroform to give a mixture of isomeric compounds having molecular formula C_4H_8O as shown below:

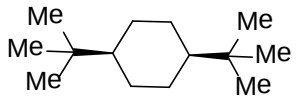


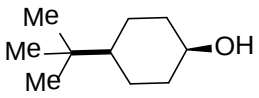
i) Label the butenes as ***E*** and ***Z***

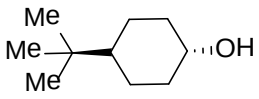
ii) How many stereoisomers are formed after hydrolysis***?***

iii) Write the structures of the products after hydrolysis in Fischer projection keeping the methyl groups along the vertical axis.

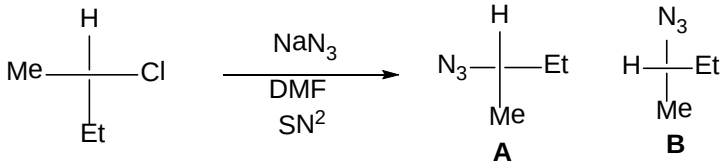
(b) Draw the most stable conformations of the following compounds. Which one of the following alcohols undergoes faster oxidation with chromic acid (H_2CrO_4) **[4]**

(i) 

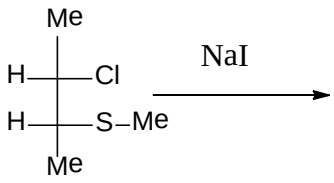
(ii) 

(iii) 

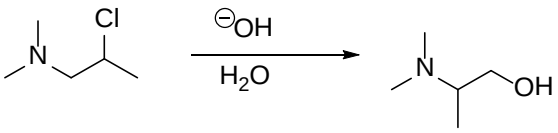
(c) Which one **A** or **B** is the correct product in the following reaction? Justify your answer. **[2]**



3. (a) Draw the correct Fisher Projection of the product in the following reaction: Explain the steps to arrive at the solution using Newman/ Sawhorse projection. **[3]**

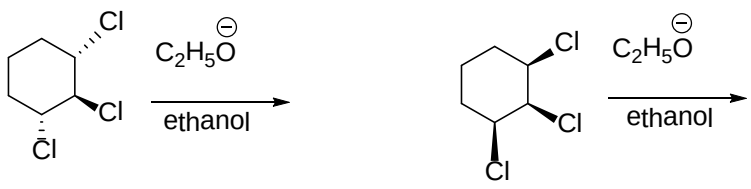


(b) Draw a mechanism for the following transformation: **[4]**

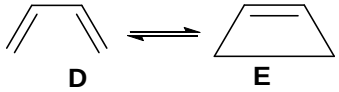


If the absolute configuration of the stereogenic center in the starting material is **S**, what will be the absolute configuration of the stereogenic center in the product? Give reasons for your answer.

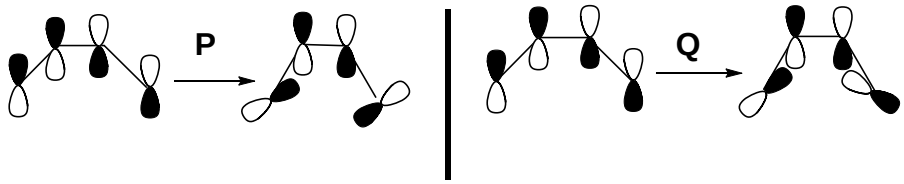
(c) Which one amongst the following compounds will undergo faster E2 elimination when treated with NaOEt and ethanol? Give reasons for your answer through conformational analysis. **[4]**



4. **(a)** The following electrocyclization process can be carried out either thermally or photochemically **[4]**



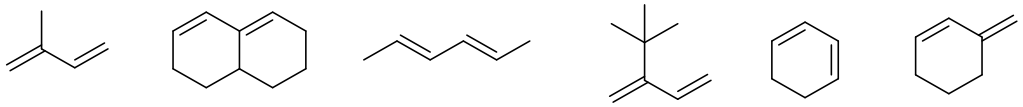
The intermediate positions of one of the π-molecular orbitals for **D** during two different cyclization processes **P** and **Q** are shown:



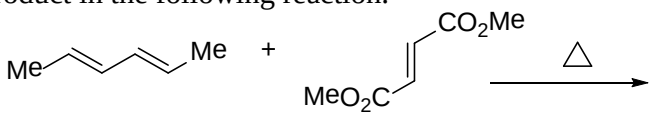
Consider the above MO picture and answer the following

(i) Which one of process **P** or **Q** denotes conrotatory ring closure?
(ii) Which one of process **P** or **Q** denotes disrotatory ring closure?
(iii) Which process **P** or **Q** will be allowed thermally? And why?

(b) Which of the following diene(s) **cannot** undergo Diels-Alder reactions? **[1]**



(c) Write the major product in the following reaction. **[2]**



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