INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR
End-Spring Semester 2016-17

Date of Examination : 25-04-2017   Session (FN/AN): <u>FN</u>   Duration <u>3 hrs</u>
Subject No. : <u>CY11001</u>   Subject Name : <u>CHEMISTRY</u>
Department/Center/School: Chemistry
Specific charts, graph paper, log book etc., required   –NA–
Special Instructions (if any): <u>Answers of Part A and Part-B should be written SEPARATELY WITHOUT MIXING and mention the question numbers while answering.</u>

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

[Given data: Atomic No.: N:7, O:8, F:9, Fe:26, Co: 27, Cu:29, Ru:44, Rh:45, Sn: 50, Ir: 77, 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; Faraday's constant: 9.648×10^3 emu; Joule's constant: 4.18 J/cal; Avogadro constant; 6.022×10^{23} mole^{-1}; Planck's constant: 6.626×10^{-34} J s; 1 eV = 1.602 $\times 10^{-19}$ J = 96.485 kJ/mol]

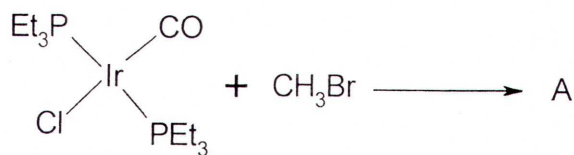1. (a) Write the Hamiltonian for H_2^+ species?   [2]

   (b) Draw a figure to show the overall potential energy variation of a simple molecule   [2]
   with bond length.

   (c) The work function of a metallic cesium is 1.14 eV. If we shine it with a light of   [2]
   700 nm wavelength, whether ejection of electrons will occur?

2. Draw molecurlar obrital diagrams for O_2^{2-} and N_2^{2-} ions and compare their bond   [3+3]
   order and bond stability with respect to their parent molecules.

3. (a) Identify bridging and chelating ligand from the following list: [2]

   Ehylenediaminetetraacetic acid, NH_3, OH⁻, Cl⁻, N_2H_4, ethylenediamine, PH_3.

   (b) Following are the data given for two complexes (complex-I and complex-II):   [3+3]

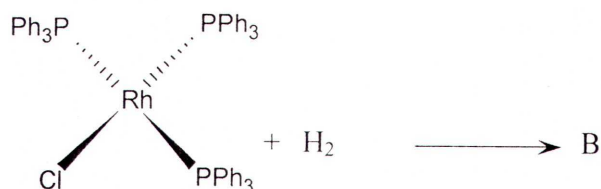|	ΔH° (kJ mol^{-1})	log β
Complex- I	-53.14	7.44
Complex- II	-56.48	10.62

   Calculate the thermodynamic parameters responsible for their formation at temperature 298 K and discuss your observations using ΔS° values.

4. (a) With the help of diagram, show both types of J-T distortion for d^2 octahedral   [5]
   complex and choose which type of distortion is preferred.

   (b) Calculate the crystal field stabilization energy (CFSE) of $[Co(H_2O)_6]^{2+}$?   [1+2]
   Give the reason for colour change of pink solution of $[Co(H_2O)_6]^{+2}$ in water to
   deep blue in conc. HCl.

5. (a) Write down the products of the following reactions (A and B) and calculate the EAN for the complexes (I and II). **[4]**
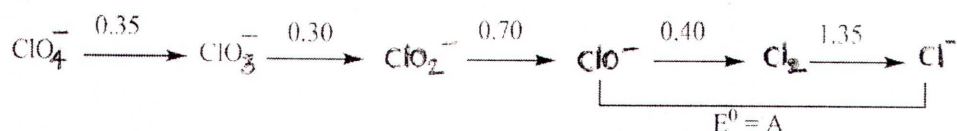
$$Et_3P\text{—}Ir(Cl)(CO)(PEt_3) + CH_3Br \longrightarrow A$$

(I)

$$Ph_3P\text{—}Rh(Cl)(PPh_3)_2 + H_2 \longrightarrow B$$

(II)

(b) Draw the structure of pre-catalyst used in Monsanto acetic acid process. **[2]**

6. (a) Answer the following questions based on the Latimer diagram for chlorine in basic solution as given below: **[2+3 +1]**

$$ClO_4^- \xrightarrow{0.35} ClO_3^- \xrightarrow{0.30} ClO_2^- \xrightarrow{0.70} ClO^- \xrightarrow{0.40} Cl_2 \xrightarrow{1.35} Cl^-$$

$$E^0 = A$$

(a) Find out the value of A (show all half reactions).

(b) Predict whether Cl_2 will undergo disproportionation reaction? Show all the half reactions and full reaction along with E^0 of the cell.

(c) Predict the strongest oxidizing agent from above.

(b) From the following standard reduction potential data predict whether Sn^{2+} will be oxidised by Fe^{3+} (with complete cell reaction)? **[2]**

$$E^0_{Fe^{3+}/Fe^{2+}} = 0.77 \text{ V} \quad \& \quad E^0_{Sn^{4+}/Sn^{2+}} = 0.15 \text{ V}$$

7. (a) (i) Draw the iron porphyrin structure. **[3+3]**

(ii) The binding of O_2 with haemoglobin is reversible, whereas the binding of CO is irreversible reaction. Explain.
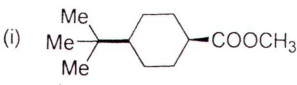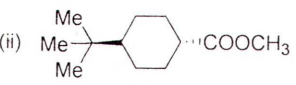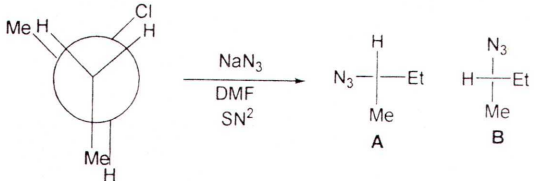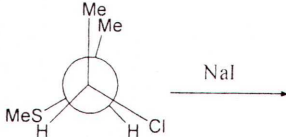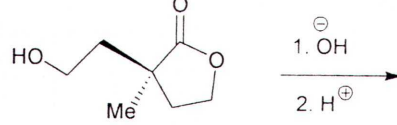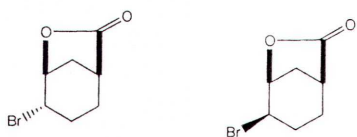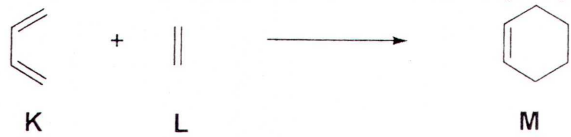
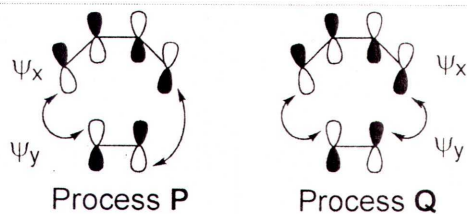(b) Why the electrical conductivity of all metals decrease with temperature? **[2]**

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

2

Part B: Organic Chemistry

Answer all the questions

1.
(a) How many stereogenic center (s) is (are) present in each of the following molecules? Assign their absolute configurations **showing the priority sequence at each centre**. **[8]**

(b) Which of the following molecules are chiral? If not then what type(s) of symmetry is (are present)? **[4]**

X contains a stereogenic centre and exist in R or S forms)

(c) Write the Fischer Projection Formulae of all possible stereoisomers of CA_4 (A is a stereogenic centre and can exist in R or S) **[3]**

Or

In the case of 2,3 dibromobutane, meso is more stable than active form. Explain this with proper justifications via Newman projections of the different conformers [assuming $\Delta S = 0$, gauche interaction value: Me/Me = 3.3 kJ/mol; Me/Br = 0.8 kJ/mol; Br/Br = 3.0 kJ/mol]

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

2.
(a) Draw trans-1,3-dimethylcyclohexane in its two chair conformations, and determine whether the two chairs are identical or enantiomers. Then do the same for the cis isomer. **[3]**

(b) Calculate the ratio of axial to equatorial methylcyclohexane that is present at room temperature (300 K). Assume $\Delta s = 0$; (R = 2 cal mol^{-1}K^{-1}; antilog(1.2) = 15.85; antilog(1.3) = 19.95, antilog(1.4) = 25.1; Boltzmann's constant = 1.38 x 10^{-23} JK^{-1}; Avogadro's number = 6.023x10^{23} mol^{-1}; 1 cal $\approx$ 4.2 J **[3]**

(c) For each of the compounds **A** through **D** indicate the number of **gauche butane interactions** present in the most stable chair conformation. **[2]**

3

(d)	Draw the most stable conformations of the following compounds. Predict with justification the rates of saponifications of the following acetates.	[4]

(i)   (ii)

(e)	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 projection.**	[3]

(b)	The following compound gives a racemic mixture upon treatment with a base followed by acidification. Draw a mechanism for the racemisation.	[4]

(c)	Among the following diastereomeric bromides, only one undergoes elimination upon treatment with a base. Write the structure of the elimination product and **also justify your answer.**	[3]

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

K   L   M

The combination of two molecular orbitals for two components **K** and **L** during two different cyclization processes **P** and **Q** are shown:

4
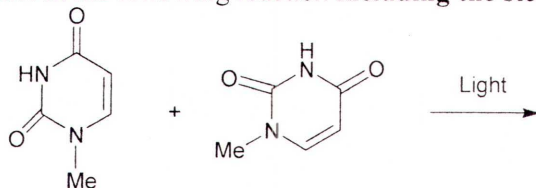
Process P   Process Q

Consider the above MO picture and answer the following

    (i) Identify the HOMO and LUMO considering molecular orbitals Ψ_x and Ψ_y.
    (ii) Which one of process **P** or **Q** denotes supra-supra ring closure?
    (iii) Which one of process **P** or **Q** denotes supra-antara ring closure?
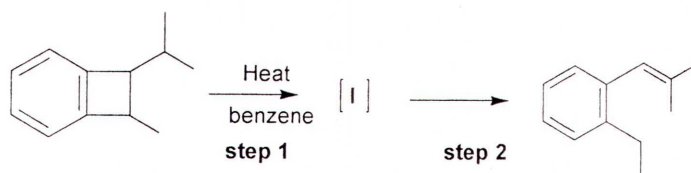   (iv) Which process **P** or **Q** will be allowed thermally?

(b) Draw the major product in the following reaction **including the stereochemistry**:   **[2]**

(c) For the following pericyclic reactions, draw the structures of the intermediate **I**. Name the types of pericyclic reactions involved in the **steps 1** and **2**.   **[3]**

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

5