M.Sc.-III/CHEM-301C/18

M.Sc. 3rd Semester Examination, 2018

CHEMISTRY

(Inorganic Chemistry)

Paper : CHEM 301C

Course ID : 31451

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five*: 2×5=10

(a) Predict the product of the following reaction (1 mole of each reactant).

(i) $[Pt(CO)Cl_3]^- + NH_3 \longrightarrow$??

(ii) $[Pt(NH_3)Br_3]^- + NH_3 \longrightarrow$??

(b) What do you mean by kinetically INERT and LABILE complexes?

(c) 'The pressure dependence of the replacement of chlorobenzene (PhCl) by piperidine in the complex $[W(CO)_4(PPH_3)(PhCl)]$ has been studied. The volume of activation is found to be + 50·3 cm^3mol^{-1}'. What does this value suggest about the mechanism?

(d) Magnetic susceptibility χ_m for a transition metal compound is measured $14{\cdot}33\times10^{-3}cm^3Kmol^{-1}$'. Fitting the susceptibility $\theta - 4{\cdot}95$ at 300K. What is Curie constant C?

(e) Define Supramolecule.

(f) Explain with example preorganisation.

(g) What are the effects of global warming?

2. Answer *any four*: 5×4=20

(a) (i) Write down the types of nucleophilic substitution in coordination complexes.

(ii) How are they related with activation parameters ($\Delta S^{\neq}$ and $\Delta V^{\neq}$)?

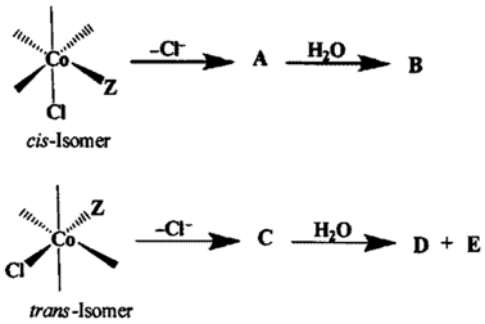
(iii) How can you determine the entropy of activation ($\Delta S^{\neq}$) (explain with equation)? 2+2+1=5

(b) (i) "$V(CO)_6$ undergoes substitution reaction by PPh_3 very fast rate, However $V(CO)_6^-$ does not react even with molten PPh_3." Explain.

(ii) Justify the statement: "Rate of hydrolysis in basic aqueous medium of $[Co(NH_3)_5Cl]^{2+}$ is much faster than $[Co(py)_5Cl]^{2+}$."

(iii) "Rate of substitution of $[Cr(H_2O)_6]^{3+}$ is very slow as compared to $[Fe(H_2O)_6]^{3+}$". —Justify. 2+2+1=5

(c) (i) Predict and explain the geometry of the intermediate and final product(s) of the following:



(ii) Arrange the following complexes in increasing order of water exchange rate: $[Sr(H_2O)_6]^{2+}$, $[Ca(H_2O)_6]^{2+}$ and $[Mg(H_2O)_6]^{2+}$. 2+3=5

(d) (i) Draw the magnetic susceptibility (χ) versus temperature (T) graph for ferromagnetic, paramagnetic and anti-ferromagnetic complexes.

(ii) When does orbital angular momentum contribute to magnetic moment? 3+2=5

(e) (i) Name three types of noncovalent interactions and explain.

(ii) What is template effect? 3+2=5

(f) (i) What is difference between pollutant and contaminant?

(ii) Write short note on Bhopal gas tragedy. 2+3=5

3. Answer *any one*: 10×1=10

(a) (i) For the reaction:

$$[R \cup (NH_3)_6]^{2+} + [Co(phen)_3]^{3+} \longrightarrow [R \cup (NH_3)_6]^{3+} + [Co(phen)_3]^{2+}$$

the observed rate constant is $1{\cdot}5 \times 10^4$ dm^3 mol^{-1} s^{-1} and the equilibrium constant is $2{\cdot}6 \times 10^5$. The rate constants for the self-exchange reactions $[R \cup (NH_3)_6]^{2+}$/ $[R \cup (NH_3)_6]^{3+}$ and $[Co(phen)_3]^{2+}$/ $[Co(phen)_3]^{3+}$ are $8{\cdot}2 \times 10^4$ and 40 dm^3 mol^{-1} s^{-1} respectively. Are these results consistent with an outer-sphere mechanism for the cross-reaction?

(ii) The compound $[Fe\,(SCN)(OH_2)_5]^{2+}$ can be detected in the reaction of $[Co\,(NCS)(NH_3)_5]^{2+}$ with Fe^{2+}(aq) to give Fe^{3+}(aq) and Co^{2+}(aq). What does this observation suggest about the mechanism?

(iii) Calculate the effective magnetic moment of $Pr^{3+}(4f^2)$.

(iv) "The effective magnetic moment $(\mu_{eff} = 5.2)$ of high spin Co^{2+} is different from spin only (μ_{so}) magnetic moment." Justify the statement with mathematical manipulation.

3+2+3+2=10

(b) (i) What is rotaxane? Give one example for synthesis of catenane.

(ii) Give one example of supramolecular catalysis.

(iii) Suggest ways how pollution caused by plastic can be reduced. (2+3)+3+2=10

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