國立臺灣師範大學107學年度碩士班招生考試試題

科目：無機化學　　適用系所：化學系

注意：1.本試題共2頁，請依序在答案卷上作答，並標明題號，不必抄題。2.答案必須寫在指定作答區內，否則依規定扣分。

1. Organometallic complexes are an important area of chemical research. Please answer the following questions regarding some organometallic compounds: (25 points)
   (a) Which of the two iron compounds $Fe(CO)_5$ and $[Fe(CO)_4(PEt_3)]$ will have the higher CO stretching frequency? Which will have the longer M–C bond?
   (b) What are so called "dihydrogen complexes"? What is the difference from dihydride complexes in terms of bonding between the metal center and hydrogen.
   (c) Explain why $[Pt(PEt_3)_2(Et)(Cl)]$ readily decomposes, whereas $[Pt(PEt_3)(Me)(Cl)]$ does not?
   (d) Explain that M–C bond is larger in the case of $NiCp_2$ compared with $FeCp_2$.

2. Draw the crystal field splitting energy diagrams of the d-metals for the following coordination complexes: (10 points)
   (a) a tetrahedral complex
   (b) a tetragonally distorted octahedral complex with z axis out.

3. Please answer the following questions regarding the complex $[Mn(NCS)_6]^{4-}$. (15 points)
   (a) Give the IUPAC name for $[Mn(NCS)_6]^{4-}$.
   (b) The magnetic moment of the complex $[Mn(NCS)_6]^{4-}$ is 6.06 μB. How many unpaired electrons does Mn have?
   (c) What is the d-electron configuration of Mn?

4. For parts (a) and (b), state which of the two solutions has the lower pH and provide your reasoning: [10 points; 2 points for your choice, and 3 points for your reasoning (no partial credit)]
   (a) 0.1M $Fe(ClO_4)_2$(aq) or 0.1M $Fe(ClO_4)_3$ (aq)
   (b) 0.1M $Ca(NO_3)_2$(aq) or 0.1M $Mg(NO_3)_2$ (aq)

5. Draw the Lewis structures (three dimensional representation) of chloric acid and chlorous acid and predict their pK_a values using Pauling's rule at acidity prediction. [10 points; 2 points for the pK_a prediction and 3 points for the Lewis structures (no partial credit)]

6. Given the following standard potentials in basic solution at room temperature:

$$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightarrow Cr(OH)_3(s) + 5OH^-(aq), E^\ominus = -0.11V$$
$$[Cu(NH_3)_2]^+(aq) + e^- \rightarrow Cu(s) + 2NH_3(aq), E^\ominus = -0.10V$$

And assuming that a reversible reaction can be established on a suitable catalyst, calculate $E^\ominus$, $\Delta_r G^\ominus$, and ln$K$ for the reductions of (a) $CrO_4^{2-}$and (b) $[Cu(NH_3)_2]^+$in basic solution. (18 points; Faraday constant = 96485 C mol^{-1})
Comment on why $\Delta_r G^\ominus$and ln$K$ are so different between the two cases despite the values of $E^\ominus$ being so similar. (4 points)

7. The stepwise formation constants for complexes of NH_3 with $[Cu(OH_2)_6]^{2+}$ (aq) are log K_{f1} = 4.15, log K_{f2} = 3.15, log K_{f3} = 2.89, log K_{f4} = 2.13, and log K_{f5} = -0.52. Suggest a reason why K_{f5} is so different. (8 points)