

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

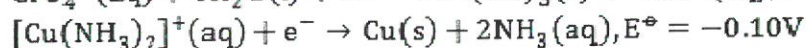
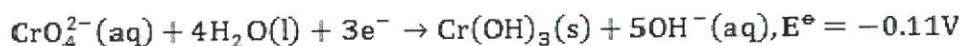
注意：1.本試題共 2 頁，請依序在答案卷上作答，並標明題號，不必抄題。2.答案必須寫在指定作答區內，否則依規定扣分。

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 $\text{Fe}(\text{CO})_5$ and $[\text{Fe}(\text{CO})_4(\text{PEt}_3)]$ 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 $[\text{Pt}(\text{PEt}_3)_2(\text{Et})(\text{Cl})]$ readily decomposes, whereas $[\text{Pt}(\text{PEt}_3)(\text{Me})(\text{Cl})]$ 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 $[\text{Mn}(\text{NCS})_6]^{4-}$. (15 points)
 - (a) Give the IUPAC name for $[\text{Mn}(\text{NCS})_6]^{4-}$.
 - (b) The magnetic moment of the complex $[\text{Mn}(\text{NCS})_6]^{4-}$ is $6.06 \mu_B$. 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 $\text{Fe}(\text{ClO}_4)_2(\text{aq})$ or 0.1M $\text{Fe}(\text{ClO}_4)_3(\text{aq})$
 - (b) 0.1M $\text{Ca}(\text{NO}_3)_2(\text{aq})$ or 0.1M $\text{Mg}(\text{NO}_3)_2(\text{aq})$

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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:



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) $[\text{Cu}(\text{NH}_3)_2]^+$ 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 $[\text{Cu}(\text{OH}_2)_6]^{2+}(\text{aq})$ 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)