91) 學年度 國立成功大學 碩士班招生考試

化學研究

無機化學

頁 試題 頁

注意事項:1. 答案一律寫在答案卷上,否則不予計分。

2. 請標明題號依序作答,不必抄題。

3. 試題應隨同試卷繳回,不得攜出試場。

1. Write formulas for the following compounds. (8%)

(a) magnesium phosphate

(b) hypochlorous acid

(c) tetraborane

(d) potassium hexacyanoferrate(III)

2. Determine the point group for each of the following species. (8%)

(a) NO_2^+ (b) SOF_4^+ (c) $B(OH)_3$ (d) $PtCl_4^{2-}$

3. Explain the following with an example: (16%)

(a) aprotic solvents

(b) n-type semiconductor

(c) S_N1CB mechanism

(d) spin-orbit coupling

4. Suggest explanations for the following facts: (24%)

- (a) The first ionization energy of atomic fluorine is greater than the first ionization energy of F₂.
- (b) Although both the Br_3^- and I_3^- ions are known, the F_3^- ion does not exist.
- (c) The conductivity of ICl is enhanced by adding either AlCl₃ or NaCl.
- (d) I₂ is purple in color as are its solutions in CCl₄ and benzene. Solutions of I₂ in acetone and diethyl ether are brown.

5. Find the number of unpaired electrons, ground state term symbols and ligand field stabilization energy for each of the following complexes. (6%)

(a) $[Fe(H_2O)_6]^{2+}$

(b) $[Cr(CN)_6]^{4-}$

6. Answer the followings:

- (a) In acid solution chromate (CrO₄²⁻) dimerizes to form the red-orange dichromate ion. Write a balanced net ionic equation for the reaction. (2%)
- (b) Given:

$$Cr^{3+} + e^{-} \longrightarrow Cr^{2+}$$
 $\varepsilon = -0.41 \text{ V}$
 $O_{2(\alpha)} + 4H^{+}(\alpha\alpha) + 4e^{-} \longrightarrow 2H_{2}O(\alpha)$ $\varepsilon = 1.23 \text{ V}$

 $O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \longrightarrow 2H_{2}O_{(l)}$ $\varepsilon = 1.23 \text{ V}$ Will acidic solutions of Cr^{2+} be stable if exposed to air, or will O_{2} oxidize Cr^{2+} to Cr^{3+} ? Show all calculation required to prove your answer. (6%)

(c) CrO₄²⁻ has T₄ symmetry. Using the group theory method, predict the possible hybridization schemes for the Cr atom in CrO₄²⁻. Which of these schemes would you expect to be most likely? Explain your answer. (8%)

T_{d}	E	8C ₃	$3C_2$	6S ₄	$6\sigma_d$		
A_{\perp}	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
							x^2-y^2
$T_{\mathbf{i}}$	3	0	-1	1	-1	$(R_{x'} R_{y'} R_{z})$ (x, y, z)	
T_{2}	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

- (d) CrO_4^{2-} ions are intense yellow but $Cr(OH)_6^{3+}$ ion is a pale-green. Characterize the origins of the transitions and explain the relative intensities. (8%)
- 7. What are Wilkinson and Ziegler-Natta catalysts, respectively? Give an example for the reactions it catalyzes for each catalyst. (8%)
- 8. Explain why Mo(PMe₃)₅H₂ is a dihydride (contains two separate H ligands), but Mo(CO)₃(PR₃)₂(H₂) contains the dihydrogen ligand. (Me = methyl, R = isopropyl). (6%)