國立成功大學

111學年度碩士班招生考試試題

編　號：78

系　所：化學工程學系

科　目：無機化學及分析化學

日　期：0219

節　次：第 2 節

備　註：可使用計算機

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※ 考生請注意：本試題可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

Part I Inorganic Chemistry (50 points)

(1) Draw the Lewis dot structure and the corresponding 3-D structure for POF_2^+ and F_2CPH. Assign the correct point group for each structure (10 pts)

(2) Sketch clear 3-D structures of all possible isomers for
   1. a trigonal prismatic complex $M(\hat{a}\hat{a})_3$, where $\hat{a}\hat{a}$ denotes a planar bidentate ligand. (5 pts)
   2. geometrical isomers of $[Co(en)(NH_3)_2Cl_2]$ that is optically active. (5 pts)

(3) Use symmetry to determine the orbital hybridization on phosphorous to describe the σ-bonds in PF_5. Note the two axial bonds are not equivalent geometrically to the three equatorial bonds. (10 pts)

(4) For a compound XY_5 with the observed vibrational frequencies for X-Y stretches (cm^{-1}):

IR:	2002, 1979
Raman:	2116, 2030, 1989

Determine which geometry, square pyramidal or trigonal bipyramidal, is consistent with the data. (10 pts)

(5) The following UV/Vis data are available for $[Ni(NH_3)_6]^{2+}$:

band	i	10700 cm^{-1}	
	ii	17500 cm^{-1}	
	iii	28300 cm^{-1}	
	iv:	15400 cm^{-1}	band iv and v are very weak
	v:	18400 cm^{-1}	

Because bands iv and v are weak, please use only bands i through iii to determine Δ and B in cm^{-1} unit (10 pts)

Part II Analytical Chemistry (50 points)

(6) Calculate the selectivity factor between two compounds, 1 and 2, whose retention volumes are 6.2 ml and 7.7 ml, respectively. The dead volume of the column used is 1.2 ml. Show that this factor is equal to the ratio of the distribution coefficients K_2/K_1 of these compounds ($t_{R(1)} < t_{R(2)}$). (10 pts)

(7) If chloroform (tricholoromethane) exhibits an infrared peak at 3018 cm^{-1} due to the C-H stretching vibration, calculate the wavenumber of the absorption band corresponding to the C-D stretching vibration in deuterochloroform. (5 pts)

(8) To determine the concentrations (mol/L) of $Co(NO_3)_2$ (compound A) and $Cr(NO_3)_3$ (compound B) in an unknown sample, the following representative absorbance data were obtained. (10 pts)

A(mol/L)	B(mol/L)	510 nm	575 nm
1.5×10^{-1}	0	0.714	0.097
0	6.0×10^{-2}	0.298	0.757
unknown	unknown	0.671	0.330

Measurements were made in 1.0 cm glass cells.

1. Calculate the four molar absorptivities: $\varepsilon_{A(510)}$, $\varepsilon_{A(575)}$, $\varepsilon_{B(510)}$, and $\varepsilon_{B(575)}$.
2. Calculate the molarities of the two salts A and B in the unknown.

(9) $Li_{1+y}CoO_2$ is an anode for high-energy-density lithium-ion batteries. Cobalt is present as a mixture of Co(III) and Co(II). Most preparations also contain inert lithium salts and moisture. To find the stoichiometry, Co was measured by atomic absorption and its average oxidation state was measured by a potentiometric titration. For the titration, 2.00 mg of solid were dissolved under N_2 in 5.000 mL containing 0.100 M Fe^{2+} in 6 M H_2SO_4 plus 6 M H_3PO_4 to give a clear pink solution:

$$Co^{3+} + Fe^{2+} \rightarrow Co^{2+} + Fe^{3+}$$

Unreacted Fe^{2+} required 3.228 mL of 0.016 M $K_2Cr_2O_7$ for complete titration. (15 pts)

1. How many mmol of Co^{3+} are contained in 25.00 mg of the material
2. Atomic absorption found 56.4 wt% of Co in the solid. What is the average oxidation state of Co?
3. Find y in the formula $Li_{1+y}CoO_2$.

(10) Calculate the voltages of the cell

$$Cu(s) \mid Cu^{2+}\ (0.030\ M) \parallel K^+Ag(CN)2^-\ (0.010\ M),\ HCN(0.10\ M),\ \text{buffer to pH } 8.21 \mid Ag(s)$$

by considering the following reactions: (10 pts)

$$Ag(CN)_2 + e^- \leftrightarrows Ag(s) + 2CN^- \qquad E^0 = -0.310\ V$$

$$Cu^{2+} + 2e^- \leftrightarrows Cu(s) \qquad E^0 = 0.339\ V$$

$$HCN \leftrightarrows H^+ + CN^- \qquad pKa = 9.21$$

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Character Table for some point groups

C_{3v} ($3m$)	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y)(R_x, R_y)$	$(x^2-y^2, 2xy)(xz, yz)$

C_{4v} ($4mm$)	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y)(R_x, R_y)$	(xz, yz)

D_{3h} $(\bar{6})m2$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xy, yz)

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, \sqrt{3}(x^2-y^2))$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		