國立成功大學

114學年度碩士班招生考試試題

編　號：60

系　所：化學工程學系

科　目：無機化學及分析化學

日　期：0210

節　次：第 2 節

注　意：1.可使用計算機
2.請於答案卷(卡)作答，於試題上作答，不予計分。

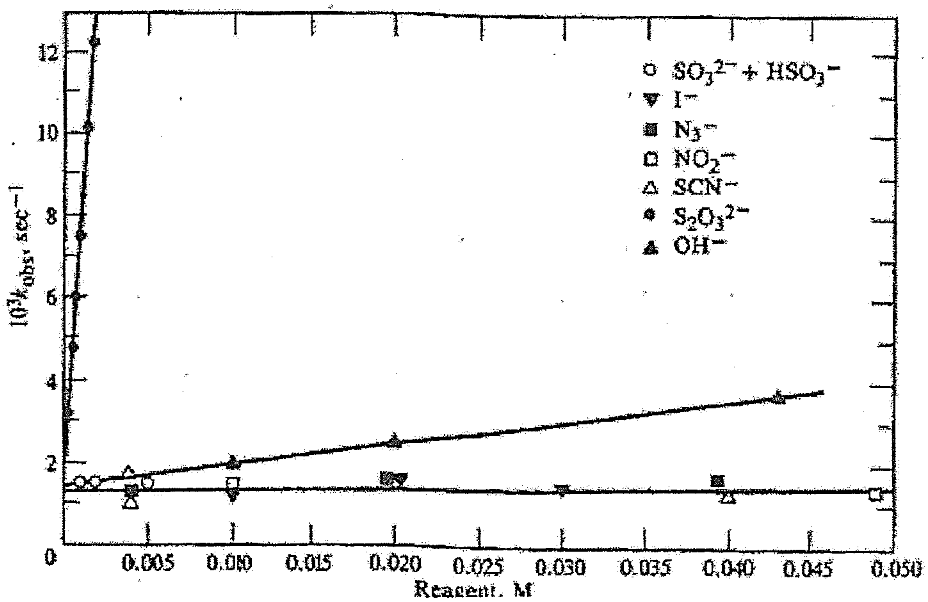
For additional information required to solve the following problems, please refer to the Appendix beginning on page 4.

1. Determine the point group and the number of IR-sctive C—O stretching vibrations for
   a. *trans*-$Fe(CO)_4Cl_2$ (5 points)
   b. *fac*-$Fe(CO)_3Cl_3$ (5 points)
   c. $Mn(CO)_5Cl$ (5 points)

2. Determine the number of unpaired electrons and the LFSE for $Fe(CN)_6^{4-}$ (5 points)

3. Give the valance electron count for the following species. Which ones obey the EAN rule? (2 points each)
   a. $Fe(CO)_4Br_2$
   b. $[Mn(CO)_5]^-$
   c. $Mn(CO)_5(CH_2C_6H_5)$
   d. $H_2Fe(CO)_4$
   e. $Rh(C_2H_4)(PPh_3)_2Cl$

4. For the reactions $[Pd(Et_4dien)Br]^+ + X^- \rightarrow [Pd(Et_4dien)X]^+ + Br^-$, a plot of observed rate constant k_{obs} versus $[X^-]$ is shown below. What mechanism can you propose to account for the zero slope when X^- = N_3^-, I^-, NO_2^-, SCN^-? And why? (10 points)



Plot of k_{obs} vs. concentration of entering neucleophile for anation of $[Pd(Et_4dien)Br]^+$ in water at 25 °C [Ref: J. B. Goddard and F. Basolo, *Inorg. Chem.* (1968) 7, 936]

5. Explain why square planar complexes of transition metals are mostly limited (other than those of planar ligands such as porphyrins) to those of **a.** d7, d8, and d9 ions (5 points) and **b.** very strong field ligands which can serve as π acceptors. (5 points)

6. The true value of a particular measurement is 131.9 μg/L. Four students (A, B, C, and D) each repeat the same procedure five times. The individual values obtained are listed below.

A	130.7	131.6	133.5	132.3	132.6	129.1
B	125.0	132.3	136.9	137.9	125.9	131.6
C	136.7	134.5	134.1	135.4	136.0	137.6
D	130.7	109.9	131.9	115.6	131.3	132.6

a. Comment the accuracy and precision of each student (12 points)

b. Suppose the results of students A and B used two apparatus, use the F test to determine if the precision of these apparatus is significantly different. (5 points)

7. The pK_a values for salicylic acid (2-hydroxybenzoic acid) are $pK_1 = 2.972$ and $pK_2 = 13.7$. How many milliliters of 0.202 M NaOH should be added to 25.0 mL of 0.023 3 M salicylic acid to adjust the pH to 3.50? (8 points)

8. Ti^{3+} is to be generated in 0.10 M $HClO_4$ solution for coulometric reduction of azobenzene ($C_6H_5N{=}NC_6H_5$).

$$TiO^{2+} + 2H^+ + e^- \leftrightarrows Ti^{3+} + H_2O \qquad E^0 = 0.100\ V$$

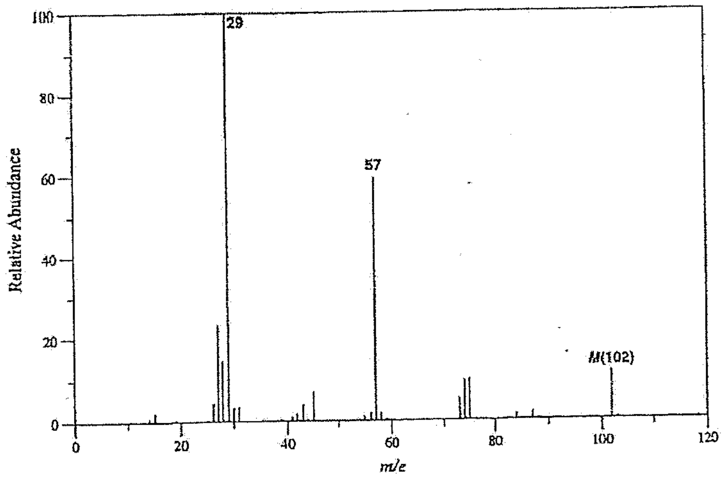
$$4Ti^{3+} + C_6H_5N{=}NC_6H_5 + 4H_2O \leftrightarrows 2C_6H_5NH_2 + 4TiO^{2+} + 4H^+$$

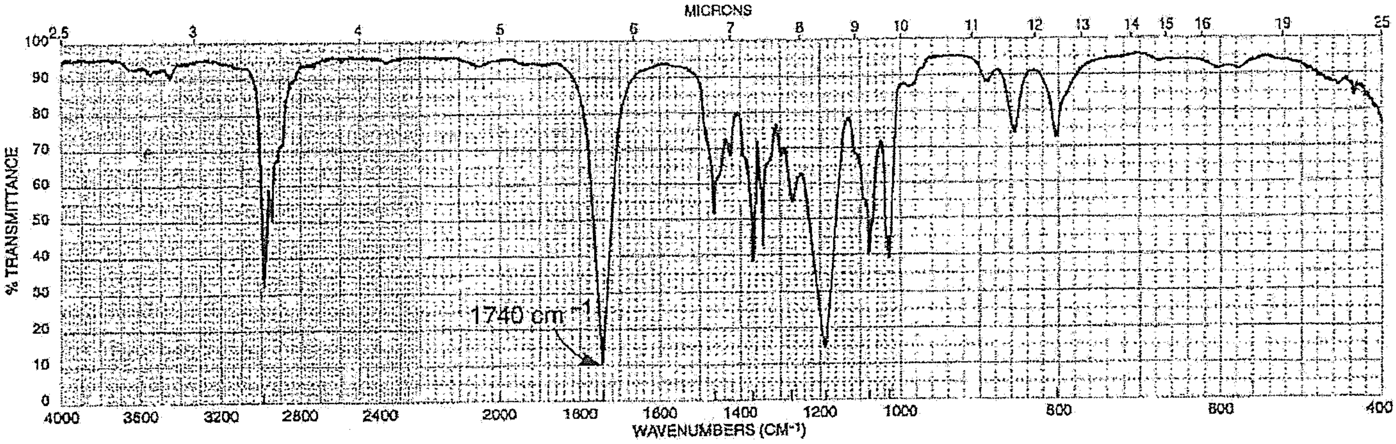
At counter electrode, water is oxidized, and O_2 is liberated at a pressure of 0.20 bar. Both electrodes are made of smooth Pt, and each as a total suface area of 1.00 cm^2. The rate of reduction of the azobenezene is 25.9 nmol/s, and the resistance of the solution between the generator is 52.4 Ω.

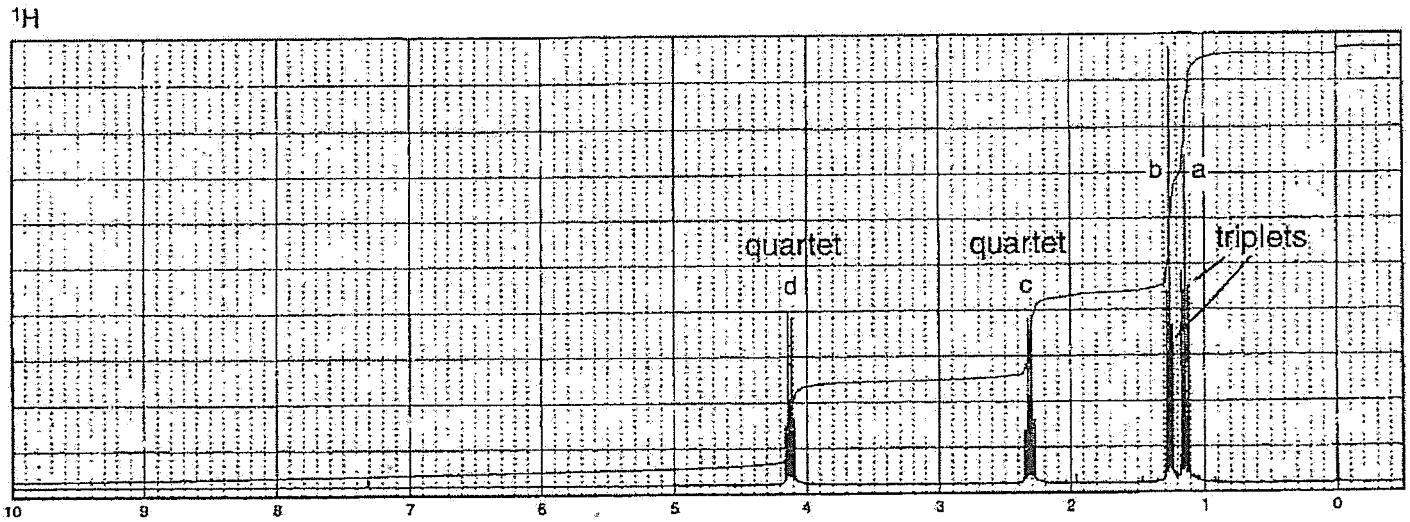
a. Calculate the cathode potential (versus S.H.E.) and the anode potential (versus S.H.E) assuming that $[TiO^{2+}]_{surface} = [TiO^{2+}]_{bulk} = 0.050$ M and $[Ti^{3+}]_{surface} = 0.10$ M. (8 points)

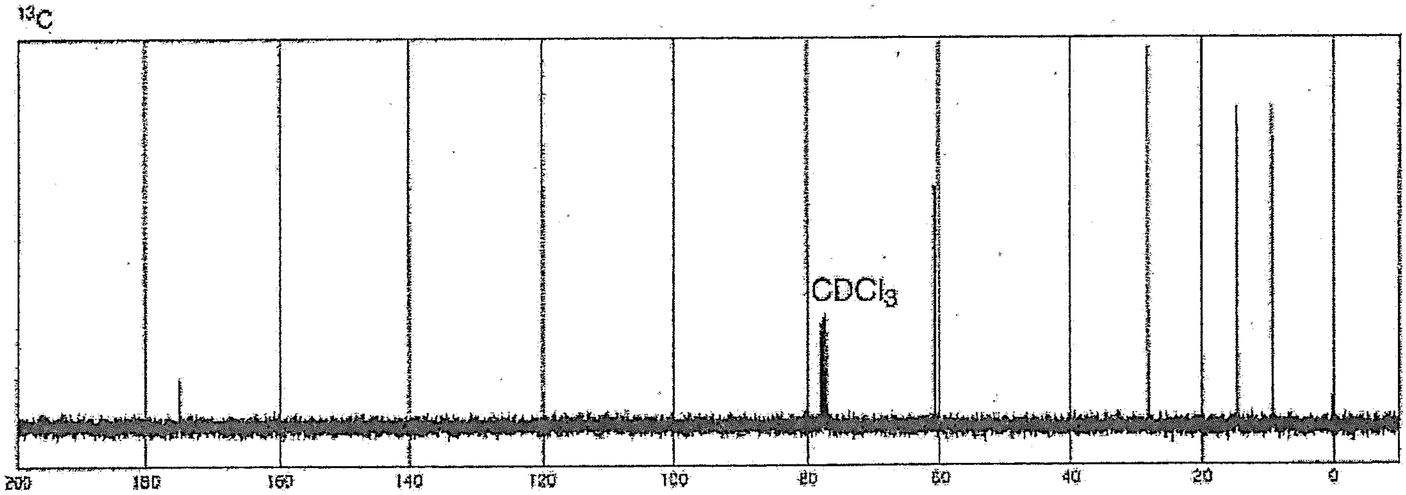
b. What should the applied voltage be? (2 points)

9. For a ester compound, the mass spectrum, IR spectrum, Proton NMR and ^{13}C NMR spectrums are given below. Determine the structure of the compound and provide your rationales. (15 points) [Ref: Pavia, D., Lampman, G. and Kriz, G. (2001) Introduction to Spectroscopy. 3rd Edi, Brooks and Cole, Washington]




MICRONS
% TRANSMITTANCE
1740 cm⁻¹
WAVENUMBERS (CM⁻¹)


¹H
quartet
d
quartet
c
b
a
triplets


¹³C
CDCl₃

Appendix

Table. The F threshold values for a confidence level of 95%

Number of measurements (denominator)	3	4	5	6	7	10	100
	Number of measurements (numerator of the fraction F)						
3	19.00	19.16	19.25	19.30	19.33	19.38	19.50
4	9.55	9.28	9.12	9.01	8.94	8.81	8.53
5	6.94	6.59	6.39	6.26	6.16	6.00	5.63
6	5.79	5.41	5.19	5.05	4.95	4.78	4.36
7	5.14	4.76	4.53	4.39	4.28	4.10	3.67
10	4.26	3.86	3.63	3.48	3.37	3.18	2.71
100	2.99	2.60	2.37	2.21	2.09	1.88	1.00

Character Table for C_{nv} (n = 2, 3, 4)

C_{2v} (2mm)	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

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)

Character Table for C_{nh} (n = 2, 3, 4)

C_{2h} (2/m)	E	C_2	I	σ_h		
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	−1	1	−1	R_x, R_y	xz, yz
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	x, y	

$\varepsilon = \exp(2\pi i/3)$

C_{3h} ($\bar{6}$)	E	C_3	C_3^2	σ_h	S_3	S_3^5		
A'	1	1	1	1	1	1	R_z	x^2+y^2, z^2
E'	1	ε	ε^*	1	ε	ε^*	(x, y)	$(x^2-y^2, 2xy)$
	1	ε^*	ε	1	ε^*	ε		
A"	1	1	1	−1	−1	−1	z	
E"	1	ε	ε^*	−1	$-\varepsilon$	$-\varepsilon^*$	(R_x, R_y)	(xz, yz)
	1	ε^*	ε	−1	$-\varepsilon^*$	$-\varepsilon$		

C_{4h} (4/m)	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	x^2+y^2, z^2
B_g	1	−1	1	−1	1	−1	1	−1		$(x^2-y^2, 2xy)$
E_g	1	i	−1	−i	1	i	−1	−i	(R_x, R_y)	(xz, yz)
	1	−i	−1	i	1	−i	−1	i		
A_u	1	1	1	1	−1	−1	−1	−1	z	
B_u	1	−1	1	−1	−1	1	−1	1		
E_u	1	i	−1	−i	−1	−i	1	i	(x, y)	
	1	−i	−1	i	−1	i	1	−i		

Character Table for D_{nh} (n = 2, 3, 4)

D_{2h} (mmm)	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

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)

D_{4h} ($4/mmm$)	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(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	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Character Table for D_{nd} (n = 2, 3, 4)

$D_{2d} = V_d$ $(\bar{4}2)m$	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		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	z	xy
E	2	0	−2	0	0	(x, y) (R_x, R_y)	(xz, yz)

D_{3d} $(\bar{3})m$	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	−1	1	1	−1	R_z	
E_g	2	−1	0	2	−1	0	(R_x, R_y)	$(x^2-y^2, 2xy)$ (xz, yz)
A_{1u}	1	1	1	−1	−1	−1		
A_{2u}	1	1	−1	−1	−1	1	z	
E_u	2	−1	0	−2	1	0	(x, y)	

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	1	1	−1	−1	R_z	
B_1	1	−1	1	−1	1	1	−1		
B_2	1	−1	1	−1	1	−1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	−2	0	0	(x, y)	
E_2	2	0	−2	0	2	0	0		$(x^2-y^2, 2xy)$
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	−2	0	0	(R_x, R_y)	(xz, yz)