（101）輔仁大學碩士班招生考試題目	考試日期：101 年 3 月 9 日　第 2 節
	本試題共　6　頁（本頁為第 1 頁）

科目：　無機化學　　系所組：化學系碩士班甲組

1. For $\mathbf{C_{2h}}$ symmetry
   a. determine the order of the $\mathbf{C_{2h}}$ group (3%)
   b. find the multiplication table of $\mathbf{C_{2h}}$ group (3%)
   c. find the possible irreducible representations (3%)
   d. find the dimensions of all irreducible representations (3%)
   e. derive the $\mathbf{C_{2h}}$ character table with x, y and z axes (3%)

2. For square $[PtCl_4]^{2-}$ ion, (D_{4h} symmetry)
   a. Show that all irreducible representations of the 3N freedom. (3 %)
   b. Classify the irreducible representations into translational, rotational, and vibrational modes. (3 %)
   c. Which vibrational modes are infrared active? (3 %)
   d. Which vibrational modes are raman active? (3 %)
   e. Which vibrational mode is silent mode? (3 %)

D_{4h}	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)	

3. Use Slater's rule to calculate the effective nuclear charges, Z*, for an electron in the 3d orbital, and in the 4s orbital of Cr. (4 %)

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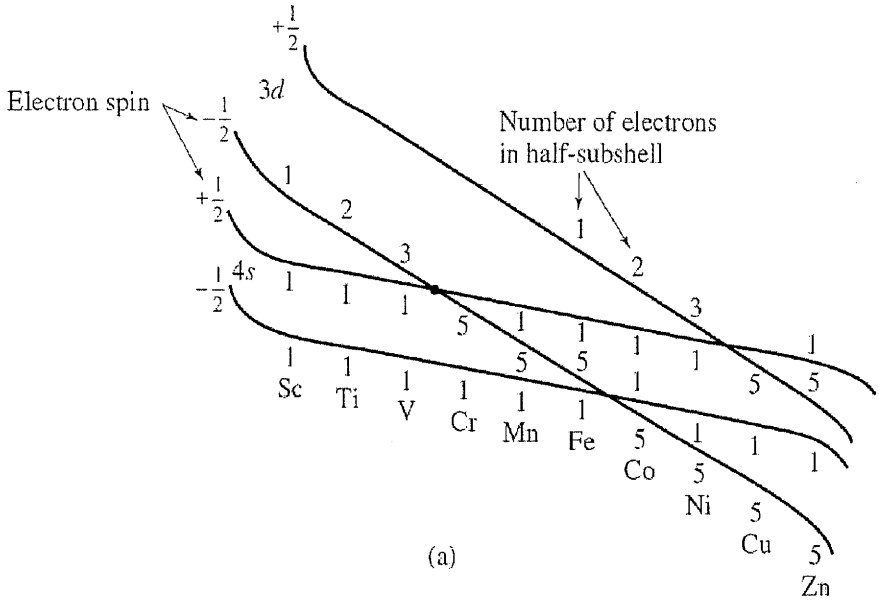
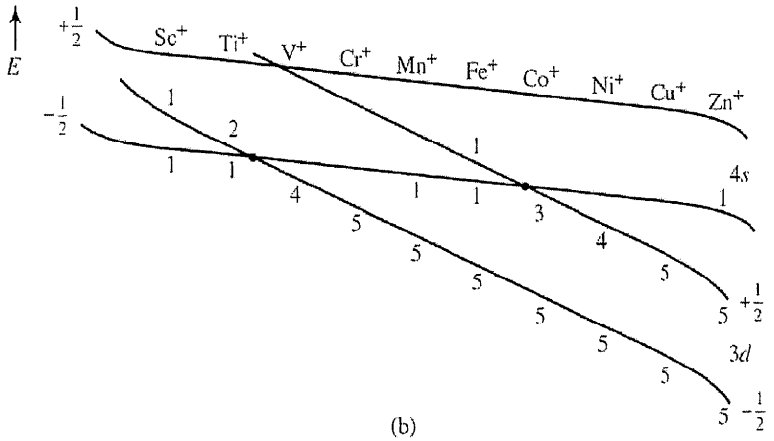
4. Give explanations of the following phenomena: (Schematic energy levels for transition metal and ion show below)
   a. The electron configuration of Cr is [Ar]$4s^1 3d^5$ rather than [Ar]$4s^2 3d^4$. (3 %)
   b. The electron configuration of Fe^+ is [Ar]$4s^1 3d^6$ rather than [Ar]$4s^2 3d^5$. (3 %)



(a)



(b)

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5. a. List the following bases in order of their base strength when reacting with H^+ in gas phase. Why?
NH_3; $NH_2(CH_3)$; $NH(CH_3)_2$; $N(CH_3)_3$; $N(C_2H_5)_3$ (5%)

b. Calculate $-\Delta H$ for the combination of H^+ with H_2O successively to produce $H^+(H_2O)_4$ by the modification of the Drago-Wayland equation
$-\Delta H = E_A E_B + C_A C_B + R_A T_B$; unit in kcal/mol (10 %)

***E* and *C* parameters for some acids and bases[a–c]**

Acid	E_A	C_A	R_A	*Acid*	E_A	C_A	R_A
I_2	0.50	2.00	—	H^+	45.00	13.03	130.21
H_2O	1.54	0.13	0.20	Li^+	11.72	1.45	24.21
H_2S	0.77	1.46	0.56	K^+	3.78	0.10	20.79
HF	2.03	0.30	0.47	NH_4^+	4.31	4.31	18.52
HCl	3.69	0.74	0.55	$(CH_3)_2NH_2^+$	3.21	0.70	20.72
HCN	1.77	0.50	0.54	$(CH_3)_3NH^+$	2.60	1.33	15.95
CH_3OH	1.25	0.75	0.39	$(CH_3)_4N^+$	1.96	2.36	8.33
C_2H_5OH	1.34	0.69	0.41	$C_5H_5NH^+$	1.81	1.33	21.72
C_6H_5OH	2.27	1.07	0.39	H_3O^+	13.27	7.89	20.01
$(CH_3)_3COH$	1.36	0.51	0.48	$(H_2O)_2H^+$	11.39	6.03	7.36
$HCCl_3$	1.49	0.46	0.45	$(H_2O)_3H^+$	11.21	4.66	2.34
HCF_3	1.32	0.91	0.27	$(H_2O)_4H^+$	10.68	4.11	−3.25
CH_3CO_2H	1.72	0.86	0.63	CH_3^+	19.70	12.61	55.09
$B(OCH_3)_3$	0.54	1.22	0.84				
$B(C_2H_5)_3$	1.70	2.71	0.61				
PF_3	0.61	0.36	0.87				
AsF_3	1.48	1.14	0.78				
SO_2	0.56	1.52	0.86				

***E* and *C* parameters for some acids and bases[a–c] (*Continued*)**

Base	E_B	C_B	T_B	*Base*	E_B	C_B	T_B
NH_3	2.31	2.04	0.56	CH_3OH	1.80	0.65	0.70
CH_3NH_2	2.16	3.12	0.59	C_2H_5OH	1.85	1.09	0.70
$(CH_3)_2NH$	1.80	4.21	0.64	C_6H_6	0.70	0.45	0.81
$(CH_3)_3N$	1.21	5.61	0.75	H_2S	0.04	1.56	1.13
$C_2H_5NH_2$	2.35	3.30	0.54	HCN	1.19	0.10	0.90
$HC(C_2H_4)_3N$	0.80	6.72	0.83	H_2O	2.28	0.10	0.43
C_5H_5N	1.78	3.54	0.73				
CH_3CN	1.64	0.71	0.83	F^-	9.73	4.28	37.40
$HC(O)N(CH_3)_2$ (dmf)	2.19	1.31	0.74	Cl^-	7.50	3.76	12.30
				Br^-	6.74	3.21	5.86
$(C_2H_5)_2O$	1.80	1.63	0.76	I^-	5.48	2.97	6.26
$O(C_2H_4)_2O$	1.86	1.29	0.71	CN^-	7.23	6.52	9.20
$(CH_3)_2SO$ (dmso)	2.40	1.47	0.65	OH^-	10.43	4.60	50.73
				CH_3O^-	10.03	4.42	33.77
$(CH_3)_2O$	1.68	1.50	0.73				
$(CH_3)_2S$	0.25	3.75	1.07				
$(CH_3)_3P$	1.46	3.44	0.90				

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6. (a) Draw a simple M.O. for $[M(L)_6]^{n+}$ type complexes in O_h system containing *s*, *p* and *d* orbitals for metal center and σ-only orbital for ligands. (4 %)
   (b) Explain the 18-electron rule for the O_h $[M(L)_6]^{n+}$ complex. (4 %)
   (c) Which of the $[Cr(NH_3)_6]^{3+}$, $[Cu(en)_3]^{2+}$, and $[Cr(CO)_6]$ complexes obey the 18-electron rule? (4%)
   (d) Explain the Jahn-Teller theorem of O_h orbitals energies (center) under tetragonal distortion for $[M(L)_6]^{n+}$ complex, containing z ligands in and z ligands out. (4 %)
   (e) The stepwise stability constants in aqueous solution at 25 °C for formation of the ions $[M(en)(H_2O)_4]^{2+}$, $[M(en)_2(H_2O)_2]^{2+}$, and $[M(en)_3]^{2+}$ for copper and nickel are given in the Table. Why is there such a difference in the third values, (4%)

	$[M(en)(H_2O)_4]^{2+}$	$[M(en)_2(H_2O)_2]^{2+}$	$[M(en)_3]^{2+}$
Cu	3×10^{10}	10^9	0.1 (estimated)
Ni	2×10^7	10^6	10^4

Character table for O_h

O_h	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		
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
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		

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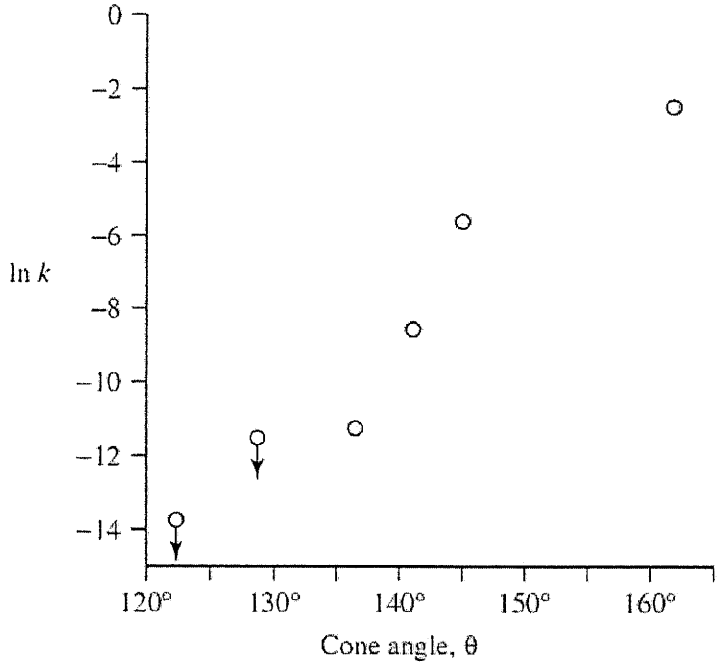
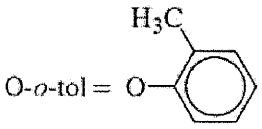
7. (a) Explain the rate constant (k) of the following reaction containing the cone angle (θ) effect of phosphine-ligand. (5 %)

$$cis\text{-}[Mo(CO)_4L_2] + CO \xrightarrow{k} [Mo(CO)_5L] + L$$

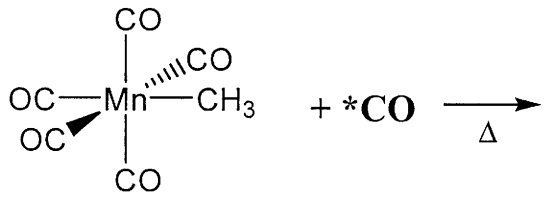


L[a]	θ	$k\ (s^{-1})$
PPh_2Cy	162°	6.40×10^{-2}
PPh_3	145°	3.16×10^{-3}
$P(O\text{-}o\text{-}tol)_3$	141°	1.60×10^{-4}
$PMePh_2$	136°	1.33×10^{-5}
$P(OPh)_3$	128°	$<1.0 \times 10^{-5}$
PMe_2Ph	122°	$<1.0 \times 10^{-6}$

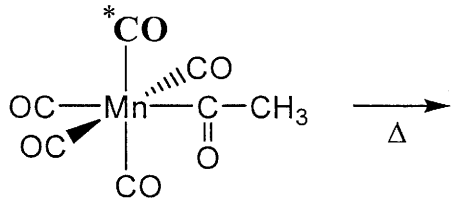
[a] Cy = cyclohexyl
Ph = phenyl
Me = methyl

O-*o*-tol = 

(b) Give the reasonable products of the following reactants (*C = ^{13}C):

(1). 

. (5 %)

(2). 

.(5 %)

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8. a. Explain the low absorption intensity of the various $[M(H_2O)_6]^{n+}$ complexes (M= first row transition metal ion, n=2 or 3). (5 %)

   b. $[Cr(H_2O)_6]^{3+}$ has absorption maxima (E) at 17,000 and 23,800 cm^{-1}. Calculate the Δ_o and B for this complex by the Tanabe-Sugano diagram (Figure 4). (5 %))

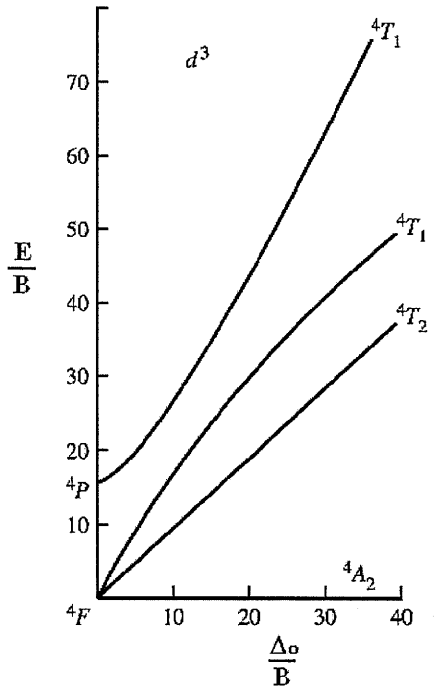

Figure 4. Tanabe-Sugano diagram of d^3 configuration.

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