國立成功大學104學年度碩士班招生考試試題

系所組別：化學系甲組

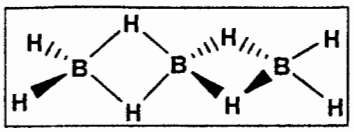
考試科目：無機化學

考試日期：0212，節次：3

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

一 選擇題 (每題 4 分)

1. What is the point group for the molecule on the right?

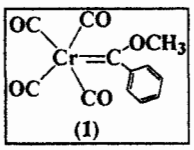


a) D_{2h} b) D_{2d} c) C_{2h} d) C_2 e) C_i

2. In general, Xe=O stretching vibration usually shows at 700-900 cm^{-1}. For XeO4 with tetrahedral structure, please determine the number of bands for Xe=O stretching in IR spectrum and Raman spectrum. (Please see the appendix for the character table)

(a) IR: 2 Raman: 2 (b) IR: 0 Raman: 2 (c) IR: 1 Raman:2 (d) IR: 3 Raman :2 (e) IR: 2 Raman:0

3. Determine the valance electron counts for complex (1) on the right.



(1)

a) 14 b) 16 c) 18 d) 20 e) 19

4. Following "question 3" , what kind of ligand does compound (1) contain? a) alkyl b) carbene c) carbyne d) cumulene e) carboxylate

5. The complexes $[Co(NH_3)_5X]^{2+}$ (X = Cl, Br, I) have charge transfer from ligand to metal bands, which of these complexes would you expect to have the highest-energy charge transfer band?

a) X = Cl b) X = Br c) X = I d) the same

6. Please use the T-S diagram for d^2 in appendix to calculate the approximate value of Δo for $[V(H_2O)_6]^{3+}$. $[V(H_2O)_6]^{3+}$ has absorption bands at 17800 and 25700 cm^{-1}.

a) 19000 cm^{-1} b) 21000 cm^{-1} c) 17000 cm^{-1} d) 22000 cm^{-1}

7. The rate constants for the exchange reaction at 0°C and 1 M $HClO_4$ are given in the table below.

$CrX^{2+} + {}^*Cr^{2+} \rightarrow {}^*CrX^{2+} + Cr^{2+}$

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*Cr is radioactive ^{51}Cr. What is the type of reaction and mechanism?
a) Substitution reaction with dissociate mechanism b) Substitution reaction with associate mechanism c) Oxidation-Reduction reaction with inner-sphere mechanism
d) Oxidation-Reduction reaction with outer-sphere mechanism

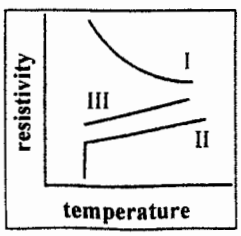
X^-	k ($M^{-1}s^{-1}$)
F^-	1.2×10^{-3}
Cl^-	11
Br^-	60
NCS^-	1.2×10^{-4}
N_3^-	>1.2

8. Determine the ground terms for the following configurations. Which statement is not correct?
(a) d^9 (D_{4h} symmetry, square planar) has the ground term of $^2D_{5/2}$ (b) d^4 (Td symmetry) has the ground term of $^5D_0$ (c) d^8 (Oh symmetry) has the ground term of $^3F_4$ (d) d^5 high spin (Oh symmetry) has the ground term of $^6D_{5/2}$

9. A six-coordinate Fe^{3+} complex with the octahedral geometry shows the magnetic moment of 1.8 μ_B. What is the most likely ligand of this complex? Please see **Table 10** in the appendix for calculated and experimental magnetic moment of some metal ions. (a) CN^- (b) Cl^- (c) H_2O (d) Br^-

10. In a primitive cubic structure where all the atoms are identical, which of the following statement is not correct? (a) the atoms occupy around 52 % of the total volume b) there is one lattice point (c) the coordination number is 6 (d) the net number of sphere in a unit cell is 2, (e) the packing is not very efficient

11. The temperature dependence of resistivity for different materials is shown on the right. Which of the following



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statement is not correct? (a) The behavior of semiconductor is shown in I. (b) The behavior of superconductor is shown in II. (c) The behavior of metal is shown in II. (d) The conductivity is better at low temperature for metals.

12. Type I copper has a very intense absorption band at 600 nm in absorption spectrum. This band is related to the binding between Cu^{2+} center and cysteine residue in the protein. Please identify the type of electron transition that results to this absorption band. (a) d-d transition (b) M → L Charge transfer (c) L→ M charge transfer (d) L → L transition

13. Which of the following protein does not contain metalloporphyrin?
(a) cytochrome c (b) P-450 (c) myoglobin (d) ferredoxin

14. Please predict the order of CO stretching frequency in IR spectrum. (a) Free CO > terminal CO > symmetric μ_3-CO > symmetric μ_2-CO (b) terminal CO > symmetric μ_3-CO > symmetric μ_2-CO > Free CO (c) symmetric μ_2-CO > symmetric μ_3-CO > terminal CO > Free CO (d) Free CO > terminal CO > symmetric μ_2-CO> symmetric μ_3-CO

15. Which of the following molecules does likely have the smallest net dipole? (a) NF_3, (b) NH_3, (c) H_2O, (d) HF

二 簡答題 (40%)

1. Regarding to $[Co(ethylenediamine)_3]^{3+}$ complex, identify the point group and construct the character table of this point group. Please answer the following questions.(20%, 每小題 2%)

	E	b	c
A_1	1	1	1
a	d	e	-1
E	2	h	i

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(1) What is the point group of this complex?
(2) What is the label "a"?
(3) What is (b, c)?
(4) What is (h, i)?
(5) What is the irreducible representation for *z* coordinate in this point group?
(6) What is the irreducible representation for *Rz* (rotation of z axis) in this point group?

(7) Please draw the possible d-orbital energy diagram for this complex (please label the orbitals).
(8) Is this complex optical active?
(9) Is this complex a paramagnetic or diamagnetic species?
(10) Please draw the ligand "ethylenediamine".

2. H_2O can act as an oxidant, reductant, acid or base, depending on the reactant. The examples are show in the following reactions. (10 % 每小題 2%)

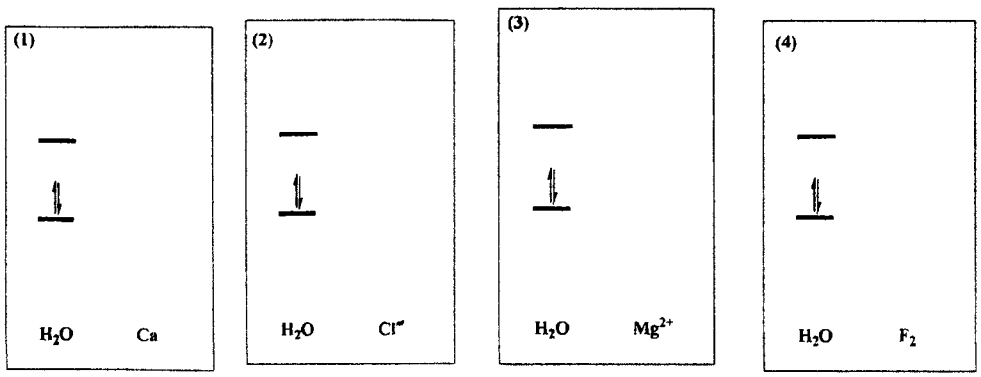
(1) $2\,H_2O + Ca \longrightarrow Ca^{2+} + 2OH^- + H_2$ (water as an oxidant)

(2) $n\,H_2O + Cl^- \longrightarrow [Cl(H_2O)n]^-$ (water as an acid)

(3) $6\,H2O + Mg^{2+} \longrightarrow [Mg(H_2O)_6]^{2+}$ (water as a base)

(4) $2\,H_2O + 2F_2 \longrightarrow 4F^- + 4H^+ + O_2$ (water as a reductant)

Please draw HOMO-LUMO interactions of water and the reactant for each reaction



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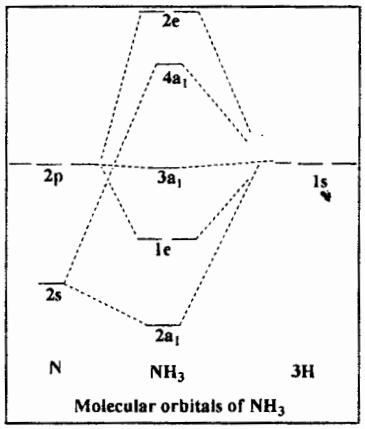
(5) When H_2O acts as a ligand and coordinates to transition metal ions, is H_2O considered as an oxidant, reductant, acid or base?

3. Please answer the questions regarding to molecular orbitals of NH_3 (shown in Figure on the right). The atomic orbitals of nitrogen are 2S, Px, Py, Pz, the atomic orbitals for three hydrogens are Sa, Sb, Sc. (10% 每小題 2%)



Molecular orbitals of NH_3

(1) What is the wave function for 2a1?
(2) What is the wave function for 2e?
(3) What is the symmetry for 3a1?
(4) What is the LUMO orbital?
(5) Please sketch for the molecular orbital of $2a_1$?

Appendix

Calculated and Experimental data for magnetic moment of some ions

Ion	n	Spin state	μs	Observed
V^{4+}	1	1/2	1.73	1.7-1.8
Fe^{3+}	1	1/2	1.73	1.7-2.2
Cu^{2+}	1	1/2	1.73	1.7-1.9
V^{3+}	2	1	2.83	2.6-2.8
Ni^{2+}	2	1	2.83	2.8-4.0
Cr^{3+}	3	3/2	3.87	3.7-3.8
Co^{2+}	3	3/2	3.87	4.1-5.2
Fe^{2+}	4	2	4.90	5.1-5.5
Fe^{3+}	5	5/2	5.92	~5.9

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Tanable-Sugano diagram for d^2

$v_1 : {}^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$

$v_2 : {}^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$

$v_3 : {}^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$

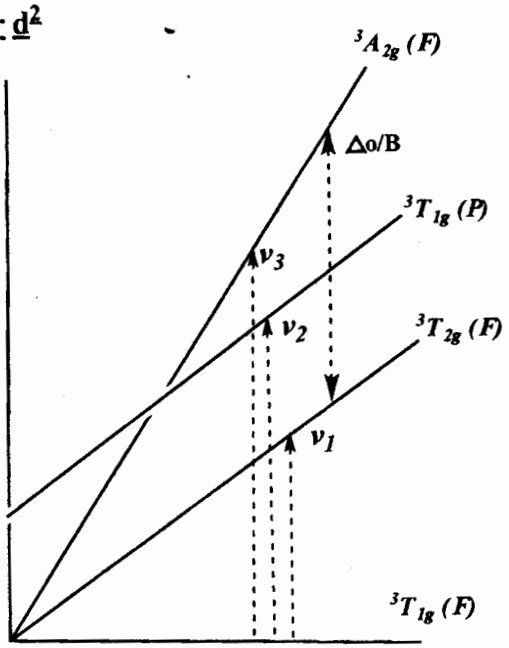
When $\Delta o/B = 31$, v_2/v_1 is aroud 1.44

For v_2:

When $\Delta o/B = 31$, E/B is around 42

For v_1:

When $\Delta o/B = 31$, E/B is around 29



Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz

Character table for C_{3v} point group

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
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, xy) (xz, yz)