

系所組別： 化學系

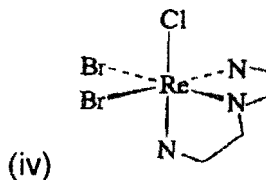
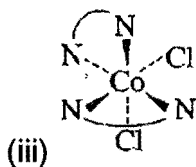
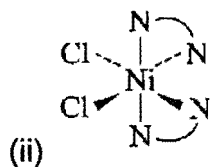
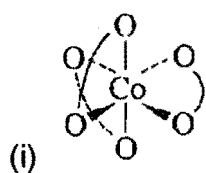
考試科目： 無機化學

考試日期： 0226，節次： 3

※ 考生請注意：本試題可使用計算機，並限「考選部核定之國家考試電子計算器」機型

一、選擇題：（40分，每題4分）

- Which of the following molecules and ions has a center of inversion, and an S_4 axis? (a) CO_2 , (b) C_2H_2 , (c) SF_4 , (d) SO_4^{2-} , (e) none of these.
- Decide the point group of a five-pointed star. (a) C_{5h} , (b) C_{5v} , (c) C_5 , (d) D_{5h} , (e) none of these.
- Decide the point group of SeF_4 molecules. (a) C_{4v} , (b) C_4 , (c) S_4 , (d) T_d , (e) none of these.
- Predict the order of solubility in water of the following species: (i) PbCl_2 (ii) PbBr_2 (iii) PbI_2 (iv) PbSe (v) PbTe . (a) (iii) > (v) > (ii) > (iv) > (i), (b) (v) > (iii) > (iv) > (ii) > (i), (c) (i) > (ii) > (iii) > (iv) > (v), (d) (v) > (iv) > (iii) > (ii) > (i), (e) none of these.
- The coulombic attraction of nearest-neighbors cations and anions accounts for the bulk of the lattice energy of an ionic compound. Estimate the order of increasing lattice energy for the following compounds. Assume that all of which crystallize in the rock-salt structure. (a) $\text{MgO} > \text{MnO} > \text{FeO} > \text{CoO}$, (b) $\text{NiO} > \text{CoO} > \text{FeO} > \text{BeO}$, (c) $\text{BeO} > \text{MgO} > \text{LiF} > \text{NaCl}$, (d) $\text{LiF} > \text{BeO} > \text{NaCl} > \text{MgO}$, (e) none of these.
- Put in order of rate of substitution by H_2O in the following complexes (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$, (ii) $[\text{Rh}(\text{NH}_3)_6]^{3+}$, (iii) $[\text{Ir}(\text{NH}_3)_6]^{3+}$, (iv) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, (v) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. (a) (iv) > (v) > (i) > (ii) > (iii), (b) (v) > (iv) > (ii) > (i) > (iii), (c) (iii) > (ii) > (i) > (v) > (iv), (d) (iv) > (v) > (i) > (ii) > (iii), (e) none of these.
- Assign the absolute configuration (Λ or Δ) to the following molecules in the order of (i), (ii), (iii) and (iv). (a) $\Delta, \Lambda, \Delta, \Lambda$, (b) $\Lambda, \Delta, \Delta, \Lambda$, (c) $\Delta, \Delta, \Delta, \Delta$, (d) $\Delta, \Delta, \Delta, \Lambda$ (e) none of these



- Determine the expected structures of the Sn_9^{4-} ion, Bi_4^{2-} ion, and Ge_9^{2-} ion in the order. (a) closo, arachno, and closo, (b) nido, arachno, nido, (c) archano, nido, nido, (d) nido, archano, closo, (e) none of these.
- Which of following species is isolobal with CH (a) $\text{Fe}(\text{CO})_3$, (b) $\text{Co}(\text{CO})_3$, (c) $\text{Ni}(\text{CO})_3$, (d) $\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_5)$, (e) none of these.

(背面仍有題目,請繼續作答)

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10. Decide the order of increasing band gap for the following compounds. (a) GaAs > GaP > ZnS > ZnO, (b) KCl > KI > CdS > CdSe, (c) AlP > AlAs > InAs > InP, (d) PbS > PbSe > KI > Si, (e) none of these.

二、簡答題：（60 分）

1. Draw the resonance structures and determine formal charges of the isomers ONCN (nitrosyl cyanide) and ONNC (isonitrosyl cyanide). Which isomer is the most stable form? (6%)
2. (a) Construct the MO for methylene CH_2 molecule. (b) Would you expect linear methylene to be diamagnetic or paramagnetic? (6%)
3. (a) In the gas phase, I_2 is violet, absorbing light near 500 nm. The I_2 dissolved in KI solution turn brown color. Explain this phenomenon by MO diagrams. (b) Explain why the triiodide ion I_3^- is linear, but I_3^+ is bent. (6%)
4. (a) A mineral crystallized in a cubic close packed (ccp) array of S^{2-} ions with Al^{3+} ion in 1/2 octahedral holes and Zn^{2+} in 1/8 tetrahedral holes. What is formula of this mineral? (b) Zinc blend ZnS has $a = 5.4307 \text{ \AA}$. Calculate the Zn-S bond length. (6%)
5. For H_2O of C_{2v} symmetry (Fig. S1) (a) Derive reducible representation for their total motions. (b) Explain the vibration is IR active or non-active. (c) Explain rotation axis R_y is antisymmetric to C_2 operation and symmetric to $\sigma_v(xz)$ operation. (6%)
6. (a) $[\text{Co}(\text{NH}_3)_6]^{2+}$ has absorption bands at 9000 and 21100 cm^{-1} . Using the Tanabe-Sugano diagram for d^7 (Fig. S2), assign the transition for the two bands and estimate values of Δ_o and B for this complex (The ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ transition is too weak to be observed). (b) MnO_4^- is a stronger oxidizing agent than ReO_4^- . Both ions have charge-transfer band; the charger-transfer band for ReO_4^- is in the ultraviolet, whereas the corresponding band for MnO_4^- is in the visible region. Are the relative energies of charge transfer absorptions consistent with the oxidizing abilities? Explain. (6%)
7. (a) Explain. The ${}^1\text{H}$ NMR spectrum of $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2$ shows two peaks of equal area at room temperature but has four resonances of relative intensity 5:2:2:1 at low temperatures. (b) For $\text{Cr}(\text{CO})_5(\text{PF}_3)$ and $\text{Cr}(\text{CO})_5(\text{PCl}_3)$, which would have the shorter C-O bonds and which would have the higher energy Cr-C stretching bands in IR spectrum. (6%)

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8. (a) Describe why tetrahedra geometry is more stable for Co(II) than for Ni(II) based on ligand field stabilization energy (LFSE) (b) Explain the effect on the d-orbital energies when an octahedral complex is stretched along the z axis. (c) Explain why the Mn–O distance in $[\text{MnO}_4]^{2-}$ is longer than in $[\text{MnO}_4]^-$. (6%)
9. Formic acid is thermodynamic unstable with respect to CO_2 and H_2 . Give a plausible mechanism for the catalysis of formic acid decomposition by $\text{IrH}_2\text{Cl}(\text{PPh}_3)_3$. (6%)
10. (a) What prevents simple iron porphyrins from functioning as O_2 carriers? (b) What is the average change in oxidation number of the Mn atoms in the proposed adamantane to cubane reaction producing O_2 in the S_4 to S_0 step in the PSII cycle? (6%)

Fig. S1

C_{2v}	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

Fig. S2

