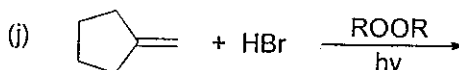
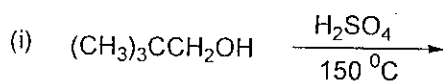
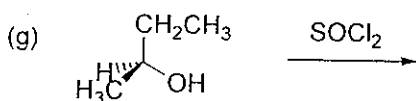
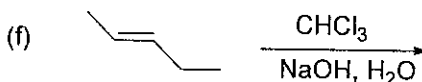
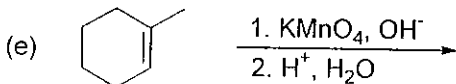
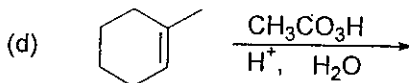
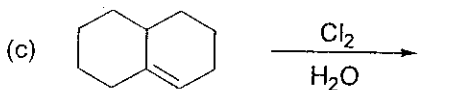
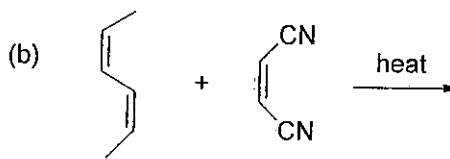
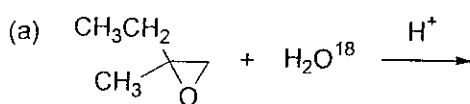


### Organic Chemistry

1. Define the following terms. (you can illustrate the term by giving example) (60pts)

- |   |   |
|---|---|
| (a) A regiospecific reaction                      | (b) Antiaromatic compounds                |
| (c) (R) and (S)-Configurations                    | (d) Endo rule in the Diels-Alder reaction |
| (e) Enantiomers                                   | (f) Diastereomers                         |
| (g) Heterolytic cleavage                          | (h) The $S_N1$ reaction                   |
| (i) Meso compound                                 | (j) Kinetic isotope effect                |
| (k) Saytzeff product from an elimination reaction |   |
| (l) Markovnikov's rule for an addition reaction   |   |
| (m) A chiral compound                             | (n) Lewis acids and bases                 |
| (o) Fisher projection                             |   |

2. Predict the major products of the following reactions. (indicate regioselectivity or stereoselectivity where relevant) (30pts)



3. Using any chemical reagent to complete the following transformations. (10pts)



8903

## 國立中山大學八十九學年度碩博士班招生考試試題

科目：化學所（無機化學）

共 一 頁 第 一 頁

## Inorganic Chemistry

(1) Counting the valence electrons on the metal atom. (16 points)

- (a)  $\text{IrBr}_2(\text{CH}_3)(\text{CO})(\text{PPh}_3)$   
 (b)  $\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\eta^6\text{-C}_6\text{H}_6)$   
 (c)  $\text{Co}_2(\text{CO})_6(\mu\text{-CO})_2$   
 (d)  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2][\text{BF}_4]$

(2) Draw the MO diagram of CO molecule and illustrate the formation of metal-CO bonding. (14 points)

(3) Heating  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$  with NaH in solution gives A, which has empirical formula  $\text{C}_7\text{H}_6\text{O}_2\text{Fe}$ . A reacts rapidly at room temperature to eliminate a colorless gas B, forming a purple-brown solid C having empirical formula  $\text{C}_7\text{H}_5\text{O}_2\text{Fe}$ . Treatment of C with iodine generates a brown solid D of empirical formula  $\text{C}_7\text{H}_5\text{O}_2\text{FeI}$ , which on treatment with  $\text{TiC}_5\text{H}_5$  gives a solid E of formula  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{Fe}$ . E, on heating, gives off a colorless gas, leaving an orange solid F of formula  $\text{C}_{10}\text{H}_{10}\text{Fe}$ . Propose structural formulas for A through F. (24 points)

(4) For the molecule  $\text{PCl}_5$ : (16 points)

- (a) Determine the possible type(s) of hybrid orbitals that can be used by P in forming  $\sigma$  bonds to the five Cl atoms.  
 (b) What type(s) of hybrid orbitals can be used in bonding to the axial chlorines? to the equatorial chlorines?  
 (c) Considering your answer to part b, explain the experimental observation that the axial P-Cl bonds (219 pm) are longer than the equatorial bonds (204 pm).

(5) Give and explain the detailed stereochemistry of the following: (15 points)

- (a)  $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$   
 (b)  $\text{Cr}_3\text{O}(\text{CH}_3\text{CO}_2)_6$   
 (c)  $\text{HCr}_2(\text{CO})_{10}^-$   
 (d)  $\text{Pt}(\text{PPh}_3)_2(\text{PhCCPh})$   
 (e)  $[(\text{RS})_4\text{Fe}_4\text{S}_4]^{2-}$

(6) Explain the following: (15 points)

- (a) The CO stretching frequencies for  $\text{V}(\text{CO})_6^-$ ,  $\text{Cr}(\text{CO})_6$ , and  $\text{Mn}(\text{CO})_6^+$  are 1859, 1981, and  $2101\text{ cm}^{-1}$ , respectively.  
 (b)  $[\text{Co}(\text{CN})_6]^{3-}$  is diamagnetic while  $\text{Co}(\text{H}_2\text{O})_6^{+3}$  is paramagnetic.  
 (c)  $[\text{CoCl}_4]^{2-}$  gives a much intense visible absorption than  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ .

國立中山大學八十九學年度碩博士班招生考試試題

科目：化學所（分析化學）

共一頁-第一頁

1. (50%) Define **five** of the following terms.

- |   |                               |
|---|-------------------------------|
| (a) blank determinations                  | (b) confidence interval       |
| (c) digestion of crystalline precipitates | (d) internal standards        |
| (e) activity coefficient                  | (f) buffer capacity           |
| (g) EDTA displacement titration           | (h) liquid-junction potential |
| (i) Michelson interferometer              | (j) half-wave potential       |

2. (30%) Answer **two** of the following questions.

- List your step-by-step procedures of preparation of a buffer solution to a desired pH.
- List your step-by-step procedures of solving multiple-equilibrium problems with a systematic method.
- Explain the reason why a complexing agent is sometimes necessary for the titration of metal cations with EDTA.

3. (20%) Explain the theory of **one** of the following techniques/instruments.

- metallic indicator electrode
- electrophoresis
- electrospray ionization
- quadrupole mass analyzers
- enzyme-linked immunosorbent assay

Physical Chemistry

1. What is the Born-Oppenheimer approximation? (10%)
2. Please show the Hamiltonian operator of hydrogen molecule. (10%)
3. The adsorption and emission spectra lines do not occur at one precise frequency, rather, the line has a measurable width. List the sources that may cause the broadening of the spectra line and discuss the way to reduce the line broadening effect. (20%)
4. Does the solubility of a solid in a liquid exhibit appreciable pressure dependence? (10%)

5. The vapor pressure of nitric acid is as follows:

T/ °C	20	40	50	70	80	90	100
P/ Torr	47.9	133	208	467	670	937	1282

What is the normal boiling point and the enthalpy of vaporization of nitric acid?

Note: Clausius-Clapeyron equation is good for this question. (20 points)

6. What is temperature? Define temperature in terms of the thermodynamic laws. (10%)
7. What is the definition of chemical potential? How is the chemical potential property applied to predict the direction of a chemical reaction? (10%)
8. "Gibbs energy" is also named as "Free energy". Why? (10%)