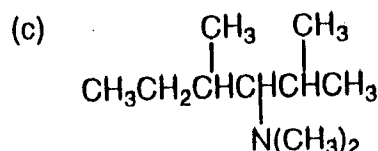
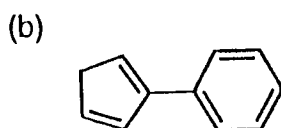
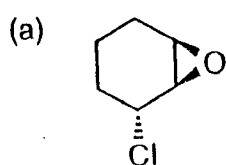


Organic Chemistry (50 pts)

1. Give the IUPAC name for the following compounds. (6 pts)

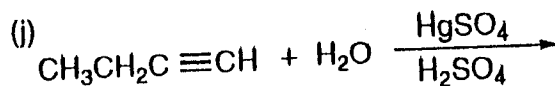
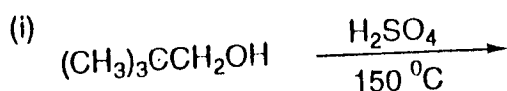
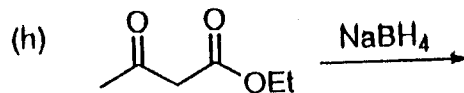
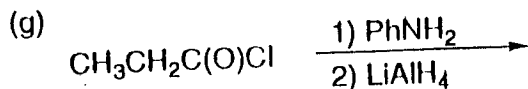
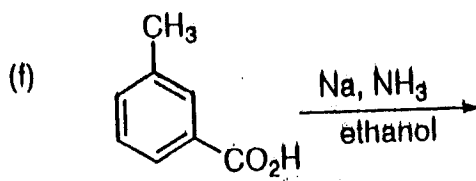
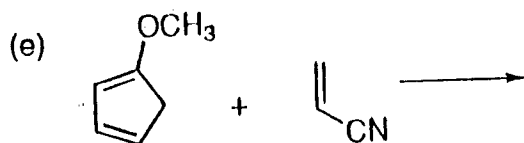
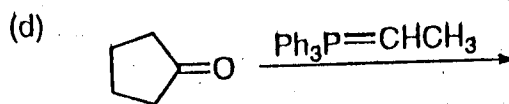
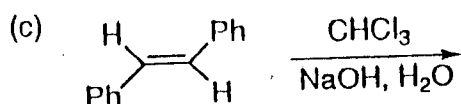
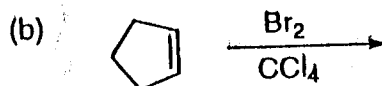
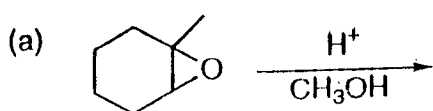


2. Give the structures of the following compounds. (4 pts)

(a) *cis*-2-Methyl-3-(1-methoxypropyl)oxirane

(b) 3-Oxo-2-propylbutanoic acid

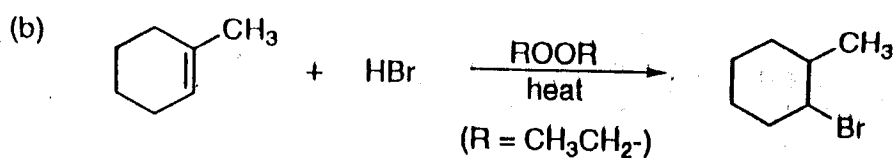
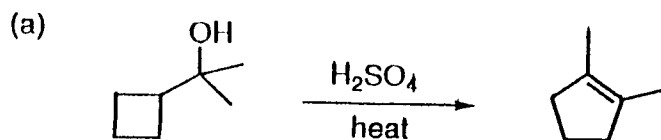
3. Write structure for the products of the following reactions. (Include stereochemistry where appropriate) (20 pts)



4. Devise methods for accomplishing the following transformations. (10 pts)



5. Write a reasonable mechanism for each of the following reactions. (10 pts)



Inorganic Chemistry (50%)

(1) Systematic construction of a $1e^-$ MO energy diagram for Oh ML_6 (including σ and π bonding). (10%)

(2) Give a brief explanation and example of the following items. (10%)

- (a) spin-orbital coupling
- (b) Jahn-Teller effect
- (c) Friedel-Crafts acylation
- (d) inner-sphere and outer-sphere electron transfer
- (e) two-electron three center bond

(3) Give and explain the detailed stereochemistry of the following: (10%)

- (a) $Mo_2(CF_3CO_2)_4$
- (b) $Cr_3O(CH_3CO_2)_6$
- (c) $HCr_2(CO)_{10}^-$
- (d) $Pt(PPh_3)_2(PhCCPh)$
- (e) $[(RS)_4Fe_4S_4]^{2-}$

(4) Explain the following: (10%)

- (a) The CO stretching frequencies for $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ are 1859, 1981, and 2101 cm^{-1} , respectively.
- (b) $[Co(CN)_6]^{3-}$ is diamagnetic while $Co(H_2O)_6^{+3}$ is paramagnetic.
- (c) $[CoCl_4]^{2-}$ gives a much intense visible absorption than $[Co(H_2O)_6]^{+2}$.

(5) (a) What is a term symbol and what information does a term symbol give? (5%)

(b) Determine the Russell-Sanders terms which arise from a d^7 electronic configuration. (5%)

化學系碩士班綜合化學

85.5.11

- 儘可能仔細地回答。務必解釋你的答案。舉出原理、定律、例子來支持你的答案。
-- 除第 3、5、6、7 題配 15 分外，其餘各題配 10 分。

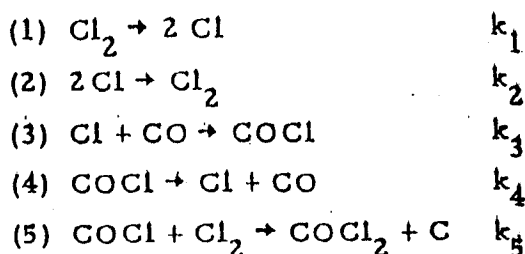
1. 課本說碘、樟腦及乾冰會昇華，設計兩種簡單的實驗來證明乾冰會昇華，也就是說它們會由固體直接變成氣體。在你的設計中要有証據證明(1)固體消失、(2)氣體生成、以及(3)沒有液體生成。
2. 承上題，水會昇華嗎？如果會，請舉一個例子。如果不會，為什麼？利用水的相圖來說明。
3. 奶粉是鮮奶脫水製成，即溶咖啡是咖啡水脫水製成，這是為了方便攜帶及長期保存。除了曬太陽及加熱之外，化學家還有許多使溶液脫水(也就是濃縮)的方法，舉出三種使溶液脫水的方法，並且詳細說明每一個方法的原理。
4. 大家都知道水是濕的，但是水為什麼是濕的呢？試由化學的觀點來解釋。並定義“濕”這一個字。
5. 什麼是動態平衡？舉出三種動態平衡的例子，並且針對每一個例子舉出它是動態平衡的証據。
6. 物理學家宣稱他們對化學實驗室也有一些貢獻，現在回想一下普通化學實驗室，舉出三利用物理原理來操作的裝置(不包括像IR, UV, NMR等儀器)，並說明其原理。
7. 早期的科學家誤認放熱過程就是自發過程，舉出三個自發吸熱過程，並由熱力學解釋造成這種錯誤的原因。
8. 舉出1995年諾貝爾化學獎得主並說明得獎原因。

--以下空白--

物理化學 (50 分)

配分：總共 7 題，除第五題八分外，其餘各題每題七分。

1. Compare in as much detail as possible the Valence-Bond and Molecular-Orbital methods of describing bonding in molecules.
2. The following mechanism for the formation of phosgene, COCl_2 , has been proposed:



(a) Use the steady state approximation to find the rate equation implied by this mechanism for the formation of COCl_2 . The rate equation may contain any or all of the constants k_1 - k_5 and the concentrations of all species other than Cl or COCl.

(b) Assume that reactions (1)-(4) are much faster than reaction (5). Show how the rate equation can be simplified in this case.

3. The classical Hamiltonian for a particle in a one-dimensional box is $H = p^2/2m$. The box has length a , with boundaries $x=0$ and $x=a$.
 - a) By expressing p as a quantum mechanical operator, transform the above classical Hamiltonian to a quantum mechanical Hamiltonian.
 - b) Write the Schrodinger equation for a particle in a one-dimensional box.
 - c) A solution to the Schrodinger equation is $\psi = C \sin Dx$. Evaluate the constants C and D .
 - d) From ψ and the Schrodinger equation determine the expression for the energy levels of the particles.

4. Molecular spectroscopy has been a fantastic tool for studying molecules on the microscopic level. In the following Table fill in the type of molecular energy involved and information which can be obtained by measuring optical spectra in each of the spectral regions.

<u>Spectral Region</u>	<u>Type of Molecular Energy</u>	<u>Information Obtained</u>
------------------------	---------------------------------	-----------------------------

Microwave

Far infrared

Infrared

Visible

Ultraviolet

5. For CO_2 gas (mass 44 amu and radius 2Å) at 25°C and 1 atmosphere pressure estimate (approximate magnitude) the following quantities.

Units must be specified where appropriate.

- Translational partition function for a single molecule.
- number of vibration degrees of freedom
- Number of rotational degrees of freedom
- number density
- average speed
- cross section
- mean free path
- diffusion coefficient
- molar entropy

6. Given the reaction $\text{A} \rightleftharpoons \text{B}$, assume both A and B behave according to the equation of state $PV = RT + P/C$, where C is a constant and is the same for both gases. Derive the relation of $K_p = \frac{P_B}{P_A}$ to ΔG° for the reaction making the usual assumptions (except gas ideality, of course). Carry the derivation through as far as possible and conclude whether K_p is independent of total pressure.

7. A. Show in detail how the free energy function $(F_T^\circ - H_0^\circ)/T$ can be obtained from purely thermal data.
- B. Show how free energy functions are used to calculate equilibrium constants. Be sure to specify any additional data required.

Analytical chemistry

1. A solution contains NaHCO_3 , Na_2CO_3 , and/or NaOH , either alone or in permissible combination. Titration of a 50.0-mL portion to a phenolphthalein end point requires 22.1 mL of 0.100 M HCl . A second 50.0-mL aliquot requires 48.4 mL of the HCl when titrated to a bromocresol green end point. Deduce the composition, and calculate the molar solute concentrations of the original solution. (for H_2CO_3 $\text{pK}_{\text{a}1} = 6.35$, $\text{pK}_{\text{a}2} = 10.3$). (6%)
2. (a) Consider an atom with **TWO AND ONLY TWO** electronic states. Draw the energy level diagrams for this atom, properly labeled, to show the difference among the processes $\Lambda\Lambda$, AE and AF . For each of these cases, what does one actually measure experimentally? Also, for each of these cases, show quantitatively how the experimental measurements relate to the concentration of the atomic species. (10%)
(b) A 50.0-mL aliquot of well water is treated with an excess of KSCN and diluted to 100.0 mL. Calculate the parts per million of iron(III) (fw = 55.847 g) in the sample if the diluted solution has an absorbance of 0.506 at 580 nm when measured in a 1.50-cm cell. At 580 nm FeSCN^{2+} has a molar absorptivity of $7.00 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$. (4%)
(c) **DISCUSS** how each of the followings environmental conditions affect the intensity of fluorescence: (i) increasing the temperature (ii) presence of oxygen. (5%)

分析化學

3. Define the following terms briefly (10%)

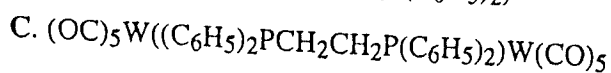
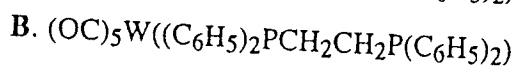
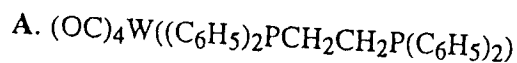
- a) isocratic elution b) reversed-phase packing
- c) eddy diffusion d) Nernst equation
- e) liquid junction potential

4. Answer the following questions briefly (15%)

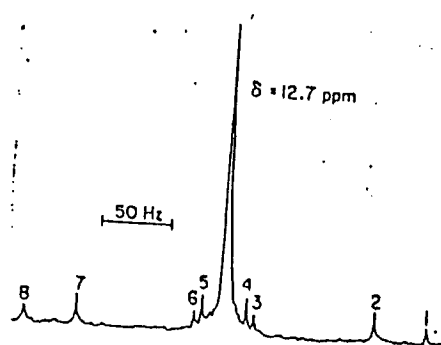
- (1) Name three commonly used detector for LC and explain respectively the principles involved.
- (2) What properties of a supercritical fluid are important in chromatography?
- (3) What does CE stand for? Explain why it becomes more and more importance in chemical analysis.
- (4) How to distinguish a limiting current and a residual current in polarography? (explain schematically)
- (5) What is the adsorptive stripping voltammetry? Why the stripping methods are applicable for trace analysis?

Inorganic Chemistry

(1) The following tungsten carbonyl complexes of diphos have been prepared.



- (a) Sketch proton decoupled ^{31}P NMR spectra for compounds A and B. ^{31}P is 100 % abundant ($I = 1/2$) and ^{183}W is 14.83 % abundant ($I = 1/2$).
- (b) The ^{31}P NMR spectrum of C is shown below. Provide an explanation for the satellite pattern.



- (2) What is the likely structure of the ion $[Mo_2(CH_3)_8]^{4-}$? What is the Mo-Mo bond order? Explain with a MO bonding model.

ANALYTICAL CHEMISTRY

For each of the following, indicate an appropriate method of quantitative analysis. Provide sufficient information so that the plan of the analytical approach and the most vital experimental conditions are apparent. Include in your description a consideration of suspected interferences and give a reasonable method for eliminating or circumventing the interferences.

Answer any four.

- ppb concentrations of chloride and sulfate in steam condensate
- Selenium in human hair
- Cadmium traces in milk powder
- Glucose, fructose and sucrose in a syrup
- Individual amino acids in a protein hydrolyzate
- Determination of dissolved oxygen as a function of depth in a lake
- Determination of percent nitrogen in an NH_4NO_3 fertilizer (5-10% N)
- Determination of Cr(VI) at the ppm level in the presence of Cr(III) in industrial waste water
- Determination of total sulfur present in "acid-rain" at less than 0.01%.