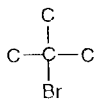
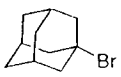
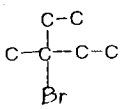
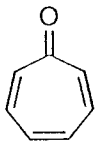
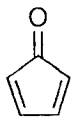
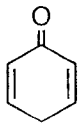
Organic Chemistry

(一)

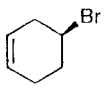
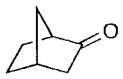
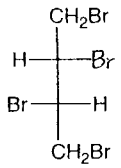
1) Which of the following compounds is not a suitable starting material for S_N1 reaction. (3%)

a) 
b) 
c) 
d) 

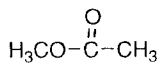
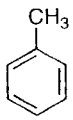
2) Which of the following compounds is relatively unstable and rapidly undergoes a Diels-Alder dimerization. (3%)

a) 
b) 
c) 
d) 

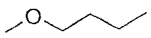
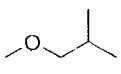
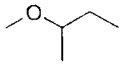
3) Which of the following compounds has no optical activity? (3%)

a) 
b) 
c) 
d) 

4) Which of the methy group in the following compounds has most downfield chemical shift in the ^1H NMR spectrum? (3%)

a) 
b) H_3C-CH_3
c) H_3C-OH
d) 

5) Which of the following compounds has less than four peaks in the ^{13}C NMR spectrum? (3%)

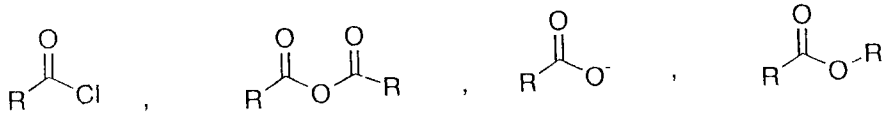
a) 
b) 
c) 
d) 

(二)

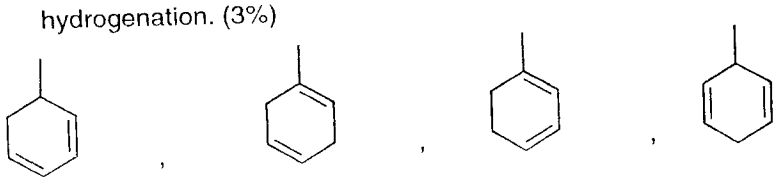
1) Arrange the following anions in order of increasing nucleophilicity. (3%)

F^-, Cl^-, Br^-, I^-

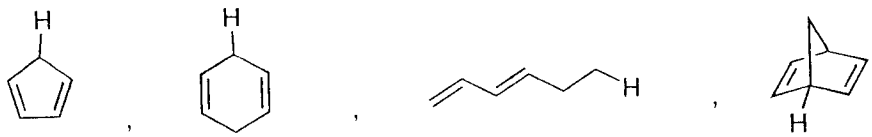
2) Arrange the following acid derivatives in order of increasing activity toward nucleophilic acyl substitution. (3%)



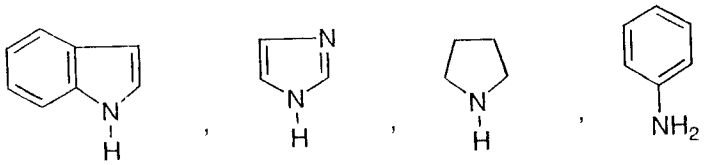
3) Arrange the following compounds in order of increasing heat of hydrogenation. (3%)



4) Arrange the following labeled hydrogens in order of increasing acidity. (3%)



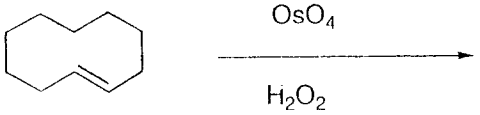
5) Arrange the following compounds in order of increasing basicity. (3%)



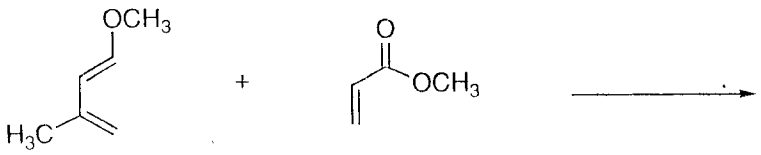
(三) Predict the products of the following reactions. Include stereochemistry where appropriate. (12%)

1).

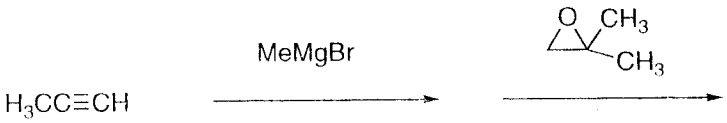
2).



3).

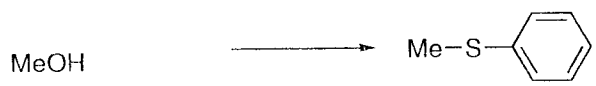


4).

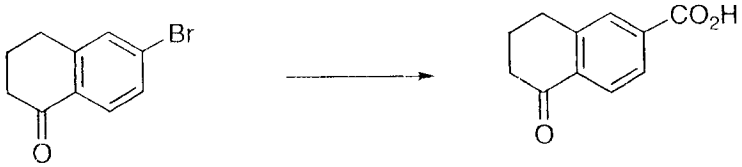


(四) Show how you would accomplish the following multi-step synthetic conversions. (8%)

1).



2).



無機化學

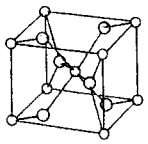
下列為資料庫，第五大題的答案都在此資料庫中。

(a)Tetradentate ligand
(b) Pentadentate ligand
(c)trans-complex
(d)mer-complex
(e)fac-complex
(f)Δ-complex
(g)Labile complex
(h)Trigonal prismatic complex
(i)Capped octahedron complex
(j)Antiprismatic complex
(k)Dodecahedron complex
(l)Linkage isomer
(m)Lewis base
(n)Leveling effect
(o)Jahn-Teller effect
(p)Berry rotation
(q)Perovskite structure
(r)Wurtzite structure
(s)Rutile structure
(t)Trigonal planar complex
(u)Electronic effect
(v)Dihedral angle
(w)Bite angle
(x)Template synthesis
(y)Superconductor
(z)Square planar complex

(五)、 配合題：(21 分)

仔細觀察下面所列出的項目後，請在上面的資料庫中，選出最能夠充分表示該項目的特性的答案。答案請以英文字母作答。

1.) $(CH_3)_2O$
2.) $Re(S_2C_2(CF_3)_2)_3]$
3) $[Co(NO_2)(NH_3)_5]^{2+}$
4) $[Ru(bipyridine)_3]^{2+}$
5.) $Fe(CO)_5$
6.) $Cr(OH_2)_6]^{2+}$
7.)



(六)、 填充題：(15 分)

1) 一般的金屬都是由礦物中以還原的方法冶煉，但是_____最先是由礦石中氧化後，再提煉而得。
2.) Pb_3O_4 、 Ag_2F 和 Na_2O 中，_____是屬於 Robin-Day Class III 的化合物。
3.) N_2O_3 、 NO 、 N_2O_5 和 N_2O_2 中，_____屬於 C_{2v} 的點群。
4.) 負型(n-type)半導體的費米能階(Fermi level)在_____能量帶附近。
5.) 氮原子的電子基態(electronic ground state term symbol)為_____。

(七)、問答題：(14 分)

1.) $[CrCl(NH_3)_5]^{2+}$ 在 220nm 附近有一吸收峰，其吸收係數約為 $10^4 Lmol^{-1}cm^{-1}$，則此峰為何種電子躍遷所產生的?請簡述理由。(5 分)

2.) 有三間倉庫分別堆放下列物質：(1)裝在鐵罐中的硝酸銨氮肥。(2)裝在紙盒 中的鋁粉。(3)裝在玻璃瓶中的四氯化碳。請問大火發生時，每間倉庫的受損情形如何?請說明理由。(9 分)

ANALYTICAL CHEMISTRY (50% total)

1. (a) Describe the preparation of 100 ml of 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37% (w/w) HCl (36.5 g/mol). (4%)
   (b) Calculate the pH of a solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl. Calculate the pH change that takes place when a 100-ml portion of 0.0500 M NaOH is added to 400 ml of this buffer solution. K_a for NH_4^+ is 5.70×10^{-10}. (5%)

2. (a) Identify and describe the major types of chemical interferences encountered in flame atomic emission and atomic absorption measurements. Discuss how each can be minimized. (12%)
   (b) Contrast molecular absorption and fluorescence measurements about selectivity and detection limits. (4%)

3. (a) Ion Chromatography (IC) has been widely used for the trace analysis of anions in water samples. Briefly explain the principle of IC. (4%)
   (b) (i) What is reverse-phase LC?
   (ii) Predict the elution order of n-hexane, n-hexanol, and n-butanol in a reverse-phase LC. Why? (5%)
   (c) FID is a common detector for GC. (i) What does FID stand for?
   (ii) Briefly explain how it works. (5%)

4. (a) Design a gas-sensing probe for carbon dioxide and briefly explain how it works. (5%)
   (b) The schematic diagram of a three-electrode potentiostat to perform linear-scan voltammetry is given in Fig 1, name the three marked electrodes in the cell and explain the role each one plays in the system. (6%)

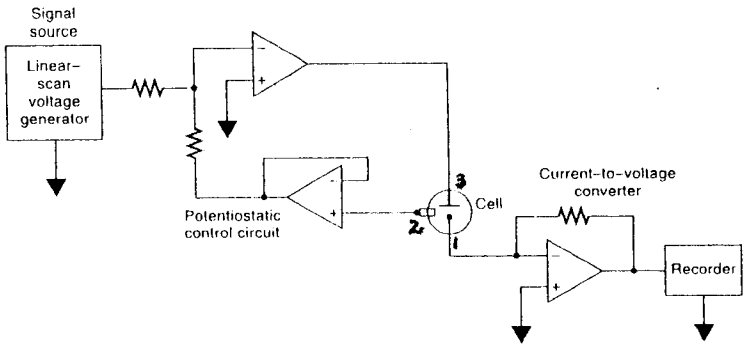


FIGURE 1 A system for potentiostatic three-electrode linear-scan voltammetry.

Physical Chemistry (50%)

5. (15 %)

a) Define in mathematical form the chemical potential of a substance in the one-phase system.

b) What is the condition for equilibrium of two phases of a one-component system?

c) The slope dP/dT of a two-phase equilibrium on a P-T phase diagram of a one-component system is given by the Clapeyron equation. Starting from the condition for phase equilibrium, derive the Clapeyron equation.

$$dP/dT = \Delta H/T\Delta V.$$

d) For water, the solid-liquid line has negative slope. Explain why this is so.

6. (15 %)

The gas-phase decomposition of ozone, $2O_3 \rightarrow 3O_2$, is believed to have the following mechanism:

$$O_3 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$

where M is any molecule.

a) Apply the steady-state (SS) approximation to O and derive the rate law.

b) Assume that rate-determining-step (RDS) approximation is applicable, derive the rate law.

c) Under what condition does the SS approximation reduce to the RDS approximation?

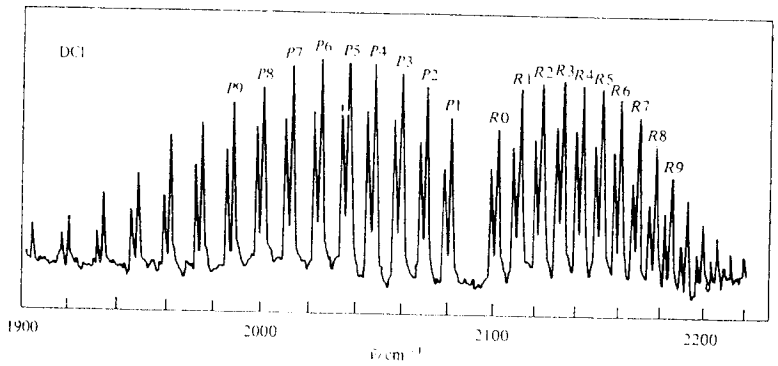
7. (10 %)

IR absorption spectrum of naturally occurring DCl is shown on next page.

a) Draw the energy level diagram to indicate the transitions correspond to the first three P branch lines, the first R branch lines and the Q branch line (not appeared in the spectrum).

b) Explain the relative line intensities within the P branch.

c) Explain why each line is a doublet.

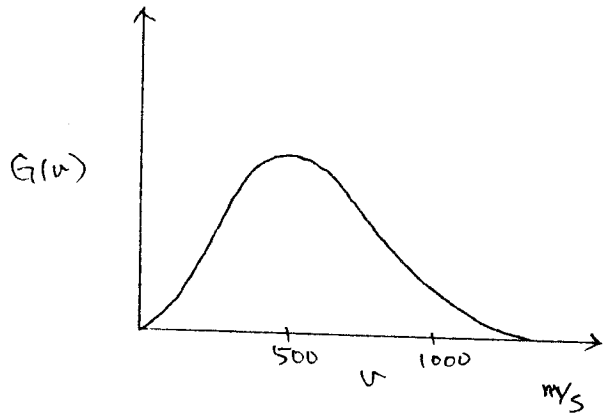


8. (10 %)

The Maxwell distribution law for speed v is

$$dN_v/N = G(v)dv = (m/2\pi kT)^{3/2} \exp(-mv^2/2kT)\, 4\pi v^2\, dv$$

and the distribution function G(v) is plotted for N_2 at 300 K below.



a) Copy the figure to your answer sheet and plot G(v) for N_2 at 600 K on this figure.

b) On a separate figure, plot G(v) for Ar, Ne, and He at 300 K.

C) On a separate figure, label the average speed <v>, the most probable speed v_{mp}, and the root-mean-square speed v_{rms} on G(v) plot.

---------- end of exam. ----------

The exam is worth a total of 100 points. Part I, true-false type, has 15 questions and each worth 2 points. Part II has 10 problems and each worth 7 points. Try to answer them in detailed and concised form. Show your work.

TRUE-FALSE QUESTIONS (30%)

1. All carbon atoms are assigned the mass of exactly 12 amu as the current standard of the atomic mass unit scale.
2. A solution of ethyl alcohol in water will conduct electricity.
3. According to Graham's law, CH_4 will diffuse faster than N_2.
4. The enthalpy of formation of $I_{2(g)}$ at 25°C and 1 atm pressure is zero.
5. No two electrons in an atom can have the same set of four quantum numbers.
6. As a rule, the metallic elements have higher ionization energies than the nonmetallic elements.
7. For the compound MgO, the difference in electronegativities is 2.3, and therefore, the bond is polar covalent.
8. BCl_3 has polar bonds but has no dipole moment.
9. The critical temperature is the lowest temperature at which a substance can exist as a liquid.
10. Increasing the temperature of a solution raises the solubility of all solid solutes.
11. The bond polarity in HF is greater than in HCl; therefore, HF is a stronger acid than HCl.
12. The equivalence point of all titrations occur at pH 7.0.
13. In general, the larger the value of K_f, the formation constant, the more stable the complex.
14. When $\Delta G^\circ=0$, the reaction is at equilibrium.
15. Nonspontaneous redox reactions can be made to occur by the application of an external voltage.

PROBLEMS (70%)

1. Sulfur forms two compounds with fluorine. In one of them 0.800 g of sulfur combines with 1.90 g of fluorine, and in the second compound 0.800 g of sulfur combines with 2.85 g of fluorine. Show that these data illustrate the law of multiple proportions and write down the formulas of these two compounds.

2. List and explain the assumptions on which the kinetic-molecular theory of gases is based and calculate the root-mean-square speed of gaseous N_2 molecules at STP. (R=8.314 J/K mol)
3. Define energy, work, heat, and state function. Consider a 9-V "alkaline" battery. Which of these three does it contain? Name a device that uses a battery to do work. Name a device that uses a battery to generate heat. Name three state functions used in thermochemistry.
4. Represent bonding in the O_2^- ion by means of a molecular orbital diagram. What is the bond order?
5. (a) In the laboratory, glassware is considered clean when water wets the glass in a continuous film. If droplets of water stand on the glass surface, the glass is considered dirty. Discuss the basis of this cleanliness test.
   (b) Why does your skin feel cool when water evaporates from it? Why will you feel warmer on a more humid summer day than on a less humid day?
6. The following data were obtained on the rate of disintegration of a pesticide in soil at 30°C.

Time(days)	11	60	93
Pesticide remaining(%)	96	80	71

   (a) What is the order of reaction with respect to pesticide concentration?
   (b) What is the value of the rate constant?
7. What changes in the equilibrium composition of the reaction

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \quad \Delta H^\circ_{rxn} = -197 \text{ kJ}$$

   will occur if it experiences the following stresses?
   (a) The partial pressure of $SO_{3(g)}$ is increased.
   (b) Inert Ar gas is added.
   (c) The temperature of the system is decreased.
   (d) The total pressure of the system is increased by reducing the available volume.
   (e) The partial pressure of $O_{2(g)}$ is decreased.
8. Describe how a buffer solution of a particular pH is made and how it operates to control pH.
9. (a) Write out the steps in the mechanism by which ozone is formed in the stratosphere.
   (b) Write out the steps in the mechanism by which ozone destruction by chlorine atoms.
   (c) What other naturally occurring molecule absorbs UV light in the stratosphere?

10. Consider a galvanic cell constructed from the following half-cells that are linked by a porous membrane: (1) an Au electrode dipped into 1.0 M $Au(NO_3)_3$; (2) an Fe electrode dipped into 1.0 M $FeSO_4$. Answer the following questions:
    (a) Which electrode is the cathode?
    (b) Write a balanced equation for the reaction occurring while the cell is discharging.
    (c) What emf should the cell generate?
    (d) In what direction will electrons flow in the outer circuit?
    (e) Toward which electrode will positive ions migrate?

    ($Fe^{2+} + 2e^- \rightarrow Fe_{(s)}$ E^o=-0.40V, $Au^{3+} + 3e^- \rightarrow Au_{(s)}$ E^o=+1.50V)