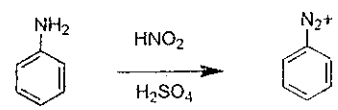
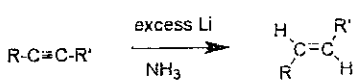
Organic Chemistry

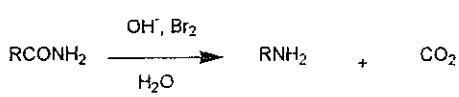
1. Explain the following terms with proper examples. (20%)
   (a) Haloform Reaction
   (b) Hofmann Elimination
   (c) Claisen Rearrangement
   (d) Nucleophilic Aromatic Substitution

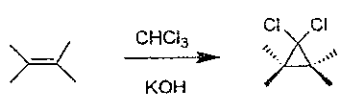
2. How to achieve the kinetic and thermodynamic control for the following reaction? Predict the products. (10%)

3. Propose reasonable mechanisms for the following reactions. (20%)

(a)


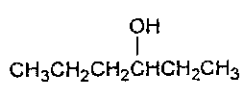
(b)


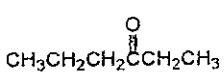
(c)


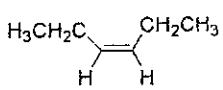
(d)


4. Use appropriate compounds no more than four carbons to synthesize the following compounds (20%)

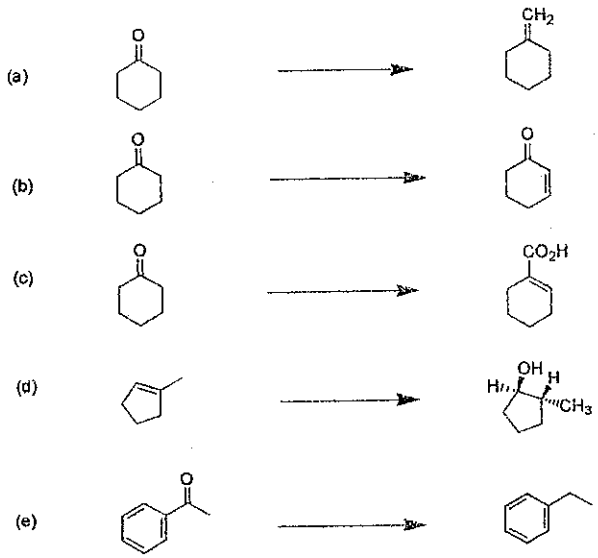
(a) $CH_3CH_2CH_2CH_2CH_2CHO$

(b)


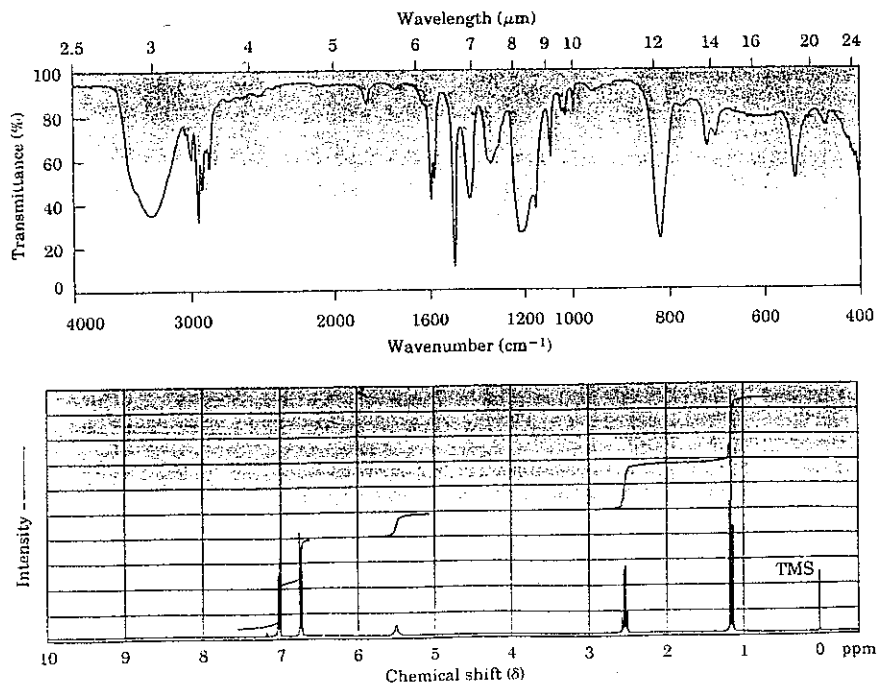
(c)


(d)


5. Use appropriate reagents to complete the following transformations. Several reagents may be needed for each transformation. (20%)



6. Compound A, $C_8H_{10}O$, has the IR and ^1H NMR spectra shown. Propose a structure with proper explanation consistent with the observed spectra. (10%)



Inorganic Chemistry

(1) (10 points) Show the molecular structures of NO_2^+, NO_2^-, and NO_2.

(2) (10 points) Explain the order of the magnitudes of the following Δ_o values for Cr(*III*) complexes in terms of the σ and π donor and acceptor properties of the ligands.

Ligand	F^-	Cl^-	H_2O	NH_3	en	CN^-
Δ_o (cm^{-1})	15,200	13,200	17,400	21,600,	21,900	33,500

(3) (15 points) In which of the following tetrahedral complexes would you expect contributions from spin-orbital coupling? (Explain briefly)
V^{3+}, Cr^{3+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}

(4) (15 points) What would the ^{19}F-NMR spectra of PCl_2F_3 look like under the following conditions? (i) Very slow fluorine exchange (ii) Faster fluorine exchange

(5) (15 points) The following carbonyl bands have been reported:
$(\eta^5\text{-}C_5H_5)Re(CO)_3$ 2024, 1937 cm^{-1}
$(\eta^5\text{-}C_5H_5)Re(CO)_2(CSe)$ 2005, 1946 cm^{-1}
On the basis of this information, which ligand, CO or CSe is the better π–acceptor? Explain briefly.

(6) (15 points) Determine the number and symmetry designations of the infrared-active O-H stretching modes in H_2O. (The x-axis is taken perpendicular to the plane.)

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

(7) (20 points) To show your understanding of basic bonding models, describe the bonding in $Cr(CO)_6$ with molecular orbital theory. (Give the MO diagrams of CO and $Cr(CO)_6$ and explain the diagrams. Hint: metal to ligand back-bonding)

Physical Chemistry

1. Compare the pressures predicted for 1 mole of n-octane confined to 20.0 dm^3 at 200 °C by the ideal gas law and by the van der Waals equation with constants a = 37.32 dm^6 atm mol^{-2} and b = 0.2368 dm^3 mol^{-1}. (10分) If the VDW equation were a better way to describe the gas under these conditions, would attractive or repulsive force prevail, and explain? (5分) 【Gas Constant R = 0.082 *l atm* mol^{-1} K^{-1}】

2. An ideal gas with C_v = 3nR expands adiabatically into a vacuum, thereby doubling its volume. Two students present the following conflicting analyses. Diana writes $T_2/T_1 = (V_1/V_2)^{R/3R}$ and $T_2 = T_1/2^{1/3}$. Wendy writes $\Delta U = q + w = 0$ and $\Delta U = C_v\Delta T$, so $\Delta T = 0$ and $T_2 = T_1$. Which student is correct? (5分) What error did the other student make? (5分) 【C_v: heat capacity at constant volume, n: number of moles T: temperature, V: volume, U: internal energy, q: heat, and w: work】

3. An adiabatic cylinder, closed at both ends, is fitted with a frictionless adiabatic piston that divides the cylinder into two parts. Initially the pressure, volume, and temperature are the same on both sides of the piston (P_o, T_o, and V_o). The gas is ideal with C_v independent of temperature and 1 mole on both sides. By means of a heating coil on the left side, heat is slowly supplied to the gas on the left until the pressure reaches $27P_o/8$. According to calculations for an adiabatic process, the final temperature on the right side is $3T_o/2$ and the final volume on the right side is $4V_o/9$. In terms of R, C_v, P_o, T_o, and V_o
   (a) What is the final temperature on the left side? (4分)
   (b) How much work is done on the gas on the right side? (4分)
   (c) How much heat must be supplied to the gas on the left side? (4分)
   (d) What is the entropy change of the gas on the right side? (4分)
   (e) What is the entropy change of the gas on the left side? (4分)

4. Consider the autocatalytic reaction

$$A \xrightarrow{k_1} B$$

$$B + A \xrightarrow{k_2} C + A$$

   (a) Assuming that the steady-state approximation is valid and that the initial concentration of A is A(0) and those of B and C are zero, develop expressions for [B], [A], and [C] as functions of time. (6分)
   (b) Under what limiting condition will the steady-state approximation be valid? (4分)
   (c) Without assuming the steady-state approximation to be valid, develop expression for [B] as a function of time. (3分)
   (d) From your general solution in part(c), verify the steady-state solution in part(a) for [B] as $t \to \infty$. (2分)

5. From undergraduate organic chemistry you are supposed to know the so-called *Hammond postulate*, which asserts that a *transition state* most closely resembles the stable species that lies closest to it in energy. Say the reaction is A + B-C → A-B + C. In light of this postulate, draw the location of the barrier on a two-dimensional *contour potential energy surface* (a plot of inter-atomic distance $d_{A\text{-}B}$ vs. $d_{B\text{-}C}$) in terms of exothermic and endothermic reactions. (10分)

6. A hydrogen-like wave function is shown below with r in units of a_0 (Bohr radius) and Z (atomic number).

$$\psi = \frac{\sqrt{2}}{81\sqrt{\pi}} \cdot Z^{3/2} \cdot (6 - Z \cdot r) \cdot Z \cdot r \cdot e^{-Zr/3} \cdot \cos\theta$$

(a) Determine the values of the quantum numbers n, l, and m_l. （10分）

(b) Determine the most probable value of r for an electron in the state specified by ψ when $Z = 1$. （10分）

7. The NH_3 molecule has C_{3v} symmetry. The Cartesian displacements of the four atoms provide a basis for the reducible 12-dimensional representation Γ_{12} of C_{3v}. After determining the characters of Γ_{12}, the representation can be reduced to $\Gamma_{12} = 2A_1 + A_2 + E$.

(a) What are the symmetries of the normal modes of vibration of NH_3? （5分）

(b) How many vibrations are infrared active? （5分）

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

(14%) 1. An emission spectroscopic method for the determination of sulfur in coal was tested by analyzing several samples of a Standard Reference Materials (SRM) from the U.S. National Institute of Standards and Technology (NIST).

(a) From the data given below, decide if a systematic error in the analyses is indicated at the 95% confidence level. Results: % S = 3.29, 3.22, 3.30, 3.23.
NIST value: % S = 3.19

(b) What is SRM?

(c) What is the systematic error?

(6%) 2. The electronic balance is widely used for weighing the mass of solid samples in an analytical laboratory. Describe the basic principle of its operation.

(14%) 3. During the titration of 50.00 mL of a 0.1000 M solution of Na_2CO_3 with a 0.2000 M solution of HCl, (given: $pK_1 = 6.35$, $pK_2 = 10.32$ for carbonic acid)

(a) calculate the pH after the addition of 45.00 mL of titrant.

(b) Calculate α_2 if the pH = 4.00. (define α_2 first)

(6%) 4. What is the chelating agent? Name one commonly used chelating agent for quantitative analysis and show its structure.

(10%) 5. (a) What does ICP stand for?

(b) Show the schematic diagram of an ICP source.

(c) Explain why the temperature as high as 8,000 K can be achieved in ICP

(10%) 6. (a) Describe the difference between a fluorescence emission spectrum and a fluorescence excitation spectrum. Also indicate which one more closely resembles an absorption spectrum. Why?

(b) Show the block diagram of an instrument for measuring fluorescence.

(10%) 7. (a) What is the low-pass filter? Show its circuit.

(b) An operational amplifier can produce an output signal that is the sum of several input signals. Design a circuit having an output given by: $v_o = -(3v_1 + 5v_2)$

(10%) 8. What electrode (in English) is commonly used for pH measurements? Show the schematic diagram of that electrode and explain how it works.

(10%) 9. (a) What is the reverse phase liquid chromatography?
(b) What is the gradient elution in LC?

(10%) 10. The scanning tunneling microscope (STM) is capable of resolving features on an atomic scale on the surface of a solid sample. Describe in detail the basic principle of STM.

Table 3-6 Values of *t* for Various Levels of Probability

Degrees of Freedom	Factor for Confidence Interval, %				
	80	90	95	99	99.9
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
11	1.36	1.80	2.20	3.11	4.44
12	1.36	1.78	2.18	3.06	4.32
13	1.35	1.77	2.16	3.01	4.22
14	1.34	1.76	2.14	2.98	4.14
∞	1.29	1.64	1.96	2.58	3.29