Final 2017

Physical Chemistry (The University of British Columbia)

This final exam consists of **16** consecutively numbered pages including **two formula sheets at the very end**. Please check that your paper is complete before starting work. **You may peel off the last two pages of formula sheets.** All work must be shown on the first **14** pages in this booklet. Only the work written on the first **14** pages will be marked; anything written on the last two pages of formula sheets will be discarded and not be marked at all.

Family Name: ______________________ First Name: ______________________
(print, surname first)

Student Number: ______________________ Signature: ______________________

University of British Columbia
CHEM 205 Final Examination
11 April 2017, 3:30−6:00 PM

Time: 2 hours 30 minutes
Answer all questions
ALL CALCULATORS ARE PERMITTED

Question	Max	Mark
Part A	20	
Part B	12	
Part C	10	
Part D	11	
Part E	9	
Part F	10	
Part G	10	
Part H	6	
Part I	12	
Total	100	

READ AND OBSERVE THE FOLLOWING EXAM RULES

1. Each examination candidate must be prepared to produce, upon the request of the invigilator or examiner, his or her UBCcard for identification.
2. Examination candidates are not permitted to ask questions of the examiners or invigilators, except in cases of supposed errors or ambiguities in examination questions, illegible or missing material, or the like.
3. No examination candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination. Should the examination run forty five (45) minutes or less, no examination candidate shall be permitted to enter the examination room once the examination has begun.
4. Examination candidates must conduct themselves honestly and in accordance with established rules for a given examination, which will be articulated by the examiner or invigilator prior to the examination commencing. Should dishonest behaviour be observed by the examiner(s) or invigilator(s), pleas of accident or forgetfulness shall not be received.
5. Examination candidates suspected of any of the following, or any other similar practices, may be immediately dismissed from the examination by the examiner/invigilator, and may be subject to disciplinary action:
   (a) speaking or communicating with other examination candidates, unless otherwise authorized;
   (b) Purposely exposing written papers to the view of other examination candidates or imaging devices;
   (c) purposely viewing the written papers of other examination candidates;
   (d) using or having visible at the place of writing any books, papers or other memory aid devices other than those authorized by the examiner(s); and
   (e) using or operating electronic devices including but not limited to telephones, calculators, computers, or similar devices other than those authorized by the examiner(s) — (electronic devices other than those authorized by the examiner(s) must be completely powered down if present at the place of writing).
6. Examination candidates must not destroy or damage any examination material, must hand in all examination papers, and must not take any examination material from the examination room without permission of the examiner or invigilator.
7. Examination candidates must follow any additional examination rules or directions communicated by the examiner(s) or invigilator(s).

Part A: [20 marks] Circle the **only one** correct answer for each of the following questions.

1. [1 mark] The energy difference between the reactants and the transition state is

1) $\Delta G_{\text{reaction}}$ 2) $\Delta H_{\text{reaction}}$ 3) $\Delta S_{\text{reaction}}$ 4) kinetic energy 5) activation energy

2. [1 mark] A cuvette filled with a green solution is placed in a spectrometer. It has been found that the intensity of the light passing through the sample is reduced by a factor of ten. Which of the following statements is true?

1) The absorbance of the green solution is 10%.

2) The absorbance of the green solution is 10.

3) The absorbance of the green solution is −1.

4) The transmittance of the green solution is 10.

5) The transmittance of the green solution is 10%.

3. [1 mark] The steps below represent a proposed mechanism for the catalyzed oxidation of CO by O_3:

Step 1: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Step 2: $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

Which of the following statements is true based on this mechanism?

1) The overall products are NO_2 and O_2.

2) The overall products are NO and CO_2.

3) The overall products are NO and O_2.

4) Either NO_2 or NO can be viewed as a catalyst.

5) Both NO_2 and NO are intermediates.

4. [1 mark] 0.01 M solutions of *t*-butanol in water and *n*-propanol in water are found to have the same osmotic pressure. This is because

1) *t*-butanol and *n*-propanol are about the same size.

2) both *t*-butanol and *n*-propanol are polar molecules and hence dissolve in water.

3) both *t*-butanol and *n*-propanol form hydrogen bonds with water.

4) at low concentration the osmotic pressure depends only on the molar concentration of the solute and not on its specific chemical nature.

5) *t*-butanol and *n*-propanol are both liquids at 25 °C and 1 atm.

5. [1 mark] An ideal gas undergoes an expansion from V_i to V_f ($V_f > V_i$) but $w = 0$ for the process. Which one of the following statements must be true?

1) The expansion was definitely reversible.

2) $\Delta U = 0$

3) The expansion was definitely irreversible.

4) $q = 0$

5) None of the above.

6. [1 mark] For the reaction, $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, the rate law is $v = k[NO_2]^2$. At a fixed temperature, if the rate is measured immediately after a small amount of CO is added to a reaction mixture that is 0.10 M in NO_2 and 0.20 M in CO, which of the following statements is true?

1) Both k and the reaction rate v remain the same.

2) Both k and the reaction rate v increase.

3) Both k and the reaction rate v decrease.

4) Only k increases; the reaction rate v remains the same.

5) Only the reaction rate v increases; k remains the same.

7. [1 mark] When 4 moles of Ne are mixed with 7 moles of Ar while holding temperature and pressure constant, which one of the following equations is true?

1) $\Delta S_{sys} > 0$ 2) $\Delta S_{sys} = 0$ 3) $\Delta S_{sys} < 0$ 4) $\Delta S_{univ} = 0$ 5) None of the above

8. [1 mark] The resonance condition that applies to several types of spectroscopy can be written as $\Delta E = hv$. Indicate the region of the electromagnetic spectrum used for NMR spectroscopy.

1) the infrared region.

2) the ultraviolet-visible region.

3) the radio frequency region.

4) the microwave region.

5) the gamma ray region.

9. [1 mark] A sample of gallium metal is sealed inside a well-insultated, rigid container. The temperature inside the container is at the melting point of gallium metal. What can be said about the energy and the entropy of the system after equilibrium has been established? Assume the insulation and rigidity prevents any energy exchange with the surroundings.

1) The total energy and the total entropy both increase.

2) The total energy and the total entropy both decrease.

3) The total energy and the total entropy both remain constant.

4) The total energy is constant; the total entropy decreases.

5) The total energy is constant; the total entropy increases.

10. [1 mark] Given the following two reactions:

$$2\,M(s) + 3\,Zn^{2+}(aq) \rightarrow 2\,M^{3+}(aq) + 3\,Zn(s), \qquad \varepsilon_1° = 0.90\text{ V}$$

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s), \qquad \varepsilon_2° = -0.76\text{ V}$$

determine the standard reduction potential for the half-reaction: $M^{3+}(aq) + 3\,e^- \rightarrow M(s)$.

1) 0.90 V 2) −1.66 V 3) 1.66 V 4) −0.62 V 5) 0.14 V

11. [1 mark] For the overall reaction, $H_2O_2(aq) + 2\,Fe^{2+}(aq) + 2\,H^+(aq) \rightarrow 2\,Fe^{3+}(aq) + 2\,H_2O(l)$, when the concentration of $H^+(aq)$ is doubled, there is no change in the reaction rate. This indicates that

1) H^+ is a spectator ion.

2) the rate determining step does not involve H^+.

3) the reaction mechanism does not involve H^+.

4) H^+ is a catalyst.

5) H^+ is an intermediate.

12. [1 mark] The reaction, $2\,Fe^{2+}(aq) + Zn(s) \rightarrow 2\,Fe^{3+}(aq) + Zn^{2+}(aq)$, is used in an electrochemical cell. The voltage measured for the cell was not equal to the calculated $\varepsilon°$ for the cell. Which of the following can cause this discrepancy?

1) The anion in the anode compartment is chloride instead of intrate as in the cathode compartment.

2) One or more of the ion concentrations is not 1 M.

3) Both of the solutions are at 25 °C instead of 0 °C.

4) The solution in the salt bridge is Na_2SO_4 instead of KNO_3.

5) None of the above.

13. [1 mark] The Second Law of thermodynamics determines if a process will be spontaneous or not. Therefore, if $\Delta S_{univ} > 0$ for a particular chemical reaction, which one of the following statements must be true?

1) $\Delta G < 0$

2) The reaction will be very fast.

3) The reaction will be fast only at the start.

4) The reaction will occur in the direction we have written, but we do not know the rate.

5) The reaction will occur slowly in the reverse direction.

14. [1 mark] The molecule Br_2 is not IR active. This is because

1) the molecule is linear.

2) halogen gases are too reactive for spectroscopy to be done.

3) the molecule has no vibrational states.

4) Br_2 is a brownish-red liquid at room temperature.

5) the molecule does not have a dipole moment.

15. [1 mark] In principle, what is the maximum number of phases that can coexist in a mixture of *t*-butanol and water?

1) 0 2) 1 3) 2 4) 3 5) 4

16. [1 mark] Consider a Donnan equilibrium across a semipermeable membrane that allows passage of water and all ions except a protein Pr^-. If at equilibrium, the system has Pr^-, Ca^{2+}, and Cl^- on side1 and Ca^{2+} and Cl^- on side 2, which of the following equations is correct?

1) Side 1: $2[Ca^{2+}] - [Cl^-] - [Pr^-] = 0$

2) Side 1: $[Ca^{2+}] - 2[Cl^-] - [Pr^-] = 0$

3) Side 2: $[Ca^{2+}] = [Cl^-]^2$

4) $\{[Ca^{2+}]^2\ [Cl^-]\}_{\text{side 1}} = \{[Ca^{2+}]^2\ [Cl^-]\}_{\text{side 2}}$

5) $\{[Ca^{2+}]\ [Cl^-]^2\ [Pr^-]\}_{\text{side 1}} = \{[Ca^{2+}]\ [Cl^-]^2\}_{\text{side 2}}$

17. [1 mark] Which one of the following statements concerning a catalyst is true?

1) It participates in the reaction mechanism.

2) It changes the equilibrium concentration of the products.

3) It does not affect a reaction energy path.

4) It always decreases the rate for a reaction.

5) It always increases the activation energy for a reaction.

18. [1 mark] When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant concentration increases

1) the average kinetic energy of molecules increases.

2) the frequency of molecular collisions increases.

3) the rate constant increases.

4) the activation energy increases.

5) the order of reaction increases.

19. [1 mark] If one mole of liquid water undergoes an adiabatic cyclic process, which one of the following statements concerning the work done on the system is correct?

1) $w > 0$ 2) $w < 0$ 3) $w = 0$ 4) $w = (3/2)\cdot RT$ 5) None of the above

20. [1 mark] In a simple voltaic (galvanic) cell, which one of the following statements correctly describes the purpose of the the salt bridge?

1) It is not necessary in order for the cell to work.

2) It acts as a mechanism to allow mechanical mixing of the solutions.

3) It allows charge balance to be maintained in the cell.

4) It acts as a membrane to block the passage of all ions.

5) It drives free electrons from one half-cell to the other.

Part B: [12 marks] At the normal sublimation point of 300 K, the heat of sublimation of lauric acid (molecular mass 200.32 g/mol) is 135.0 kJ/mol. The molar heat capacities of the solid and gasous forms of lauric acid are $C_{p,m}$(solid) = 360.58 J K^{-1} mol^{-1} and $C_{p,m}$(gas) = 931.17 J K^{-1} mol^{-1}, respectively. Under 1 atm pressure, when a sample of 100.0 g solid lauric acid is brought to a temperature of 600 K, the sample immediately sublimates. Calculate the changes in enthalpy and entropy of this process in the sample.

Part C: [10 marks] One mole of a monatomic ideal gas ($C_{v,m} = 3R/2$) initially at 300 K undergoes an adiabatic expansion against a constant external pressure of 2 atm increasing its volume from 1 L to 2 L.

(a) [8 marks] Calculate w, q, ΔU, ΔH, ΔS, ΔS_{surr}, and the final temperature T_f of the gas for this process.

(b) [2 marks] Is this process spontaneous? (circle the **only one** correct answer below)
Explain your answer.

1) Yes 2) No 3) Not enough information to know the answer.

Part D: [11 marks] Answer the following questions for the reaction occurring in aqueous, basic solution:

$$I^-(aq) + OCl^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$$

(a) [5 marks] The initial rate of the reaction was studied and was shown to depend on $[I^-]_0$, $[OCl^-]_0$, and $[OH^-]_0$. Based on the following available data, determine the rate law and the rate constant.

Experiment	$[I^-]_0$ (M)	$[OCl^-]_0$ (M)	$[OH^-]_0$ (M)	Initial Rate (M/s)
#1	2.0×10^{-3}	1.5×10^{-3}	1.00	1.8×10^{-4}
#2	4.0×10^{-3}	1.5×10^{-3}	1.00	3.6×10^{-4}
#3	2.0×10^{-3}	3.0×10^{-3}	2.00	1.8×10^{-4}
#4	4.0×10^{-3}	3.0×10^{-3}	1.00	7.2×10^{-4}

(b) [6 marks] This reaction has the following proposed mechanism with rate constants k_1, k_2, k_3, and k_4:

$$\begin{cases} \text{Step 1:} & OCl^-(aq) + H_2O(l) \rightarrow HClO(aq) + OH^-(aq) & k_1 \\ \text{Step 2:} & HClO(aq) + OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l) & k_2 \\ \text{Step 3:} & I^-(aq) + HClO(aq) \rightarrow HIO(aq) + Cl^-(aq) & k_3 \\ \text{Step 4:} & HIO(aq) + OH^-(aq) \rightarrow OI^-(aq) + H_2O(l) & k_4 \end{cases}$$

Using the **steady state approximation** and treating H_2O concentration as a constant, derive the rate law expression for this reaction based on this mechanism.

$$v = -\frac{d[OCl^-]}{dt} =$$

Part E: **[9 marks]** The enzyme catalase catalyzes the decomposition of hydrogen peroxide (H_2O_2), with an activation energy E_a = 8.4 kJ/mol. The following data are obtained regarding the rate of reaction as a function of substrate concentration:

$[H_2O_2]_0$ (M)	0.002	0.005
Initial Rate (M/s)	2.76×10^{-3}	6.00×10^{-3}

The concentration of catalase is 3.5×10^{-9} M. Use these data to answer the following questions.

(a) [6 marks] Determine the maximum reaction rate v_{max}, the Michaelis constant K_M, and the rate constant k_b for the final product formation step of this enzyme catalyzed reaction.

(b) [3 marks] It has been found that the rate constant of this enzyme catalyzed reaction increases by a factor of 1.50 from 10 °C to a higher final temperature. Determine this final temperature.

Part F: **[10 marks]** At 37 °C, a solution of aluminum acetate, $Al(CH_3COO)_3 = Al^{3+} + 3\,CH_3COO^-$, is separated by a semipermeable membrane. Outside the cell, a triple-charged protein ion (whose counterion is either Al^{3+} or CH_3COO^-) is also present. The membrane is selectively permeable to everything in the system except for the protein ion. The equilibrium concentrations of CH_3COO^- inside the cell and Al^{3+} outside the cell are 60.0 mM and 50.0 mM, respectively.

(a) [5 marks] Calculate the equilibrium concentrations of CH_3COO^- outside the cell and Al^{3+} inside the cell.

(b) [1 mark] Is the protein ion positively or negatively charged? (circle the only one correct answer below)

1) Positively charged 2) Negatively charged 3) Charge neutral

(c) [2 marks] Calculate the equilibrium concentration of the protein ion outside the cell.

(d) [2 marks] Calculate the absolute value of the Donnan potential across the cell membrane after the equilibrium is reached.

Part G: [10 marks] We know the following standard reduction potentials at 298 K:

$$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s) \qquad \varepsilon_1° = -0.440\text{ V}$$
$$Fe^{3+}(aq) + 3\,e^- \rightarrow Fe(s) \qquad \varepsilon_2° = -0.0363\text{ V}$$

(a) [3 marks] In the empty boxes below, write the overall cell reaction in the direction of spontaneous change and write out the actual reactions (*i.e.*, reduction and oxidation) occurring at the electrodes.

Anode (Oxidation)	
Cathode (Reduction)	
Total Cell Reaction	

(b) [3 marks] Calculate $\Delta G°$ and the standard cell potential $\varepsilon°$ for the total cell reaction.

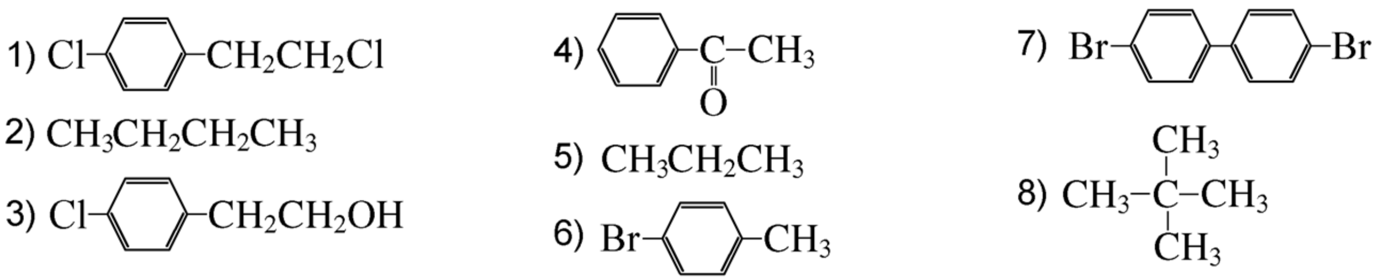
(c) [4 marks] Given the following half-cell reaction at 298 K for the low-insolubility base $Fe(OH)_2(s)$:

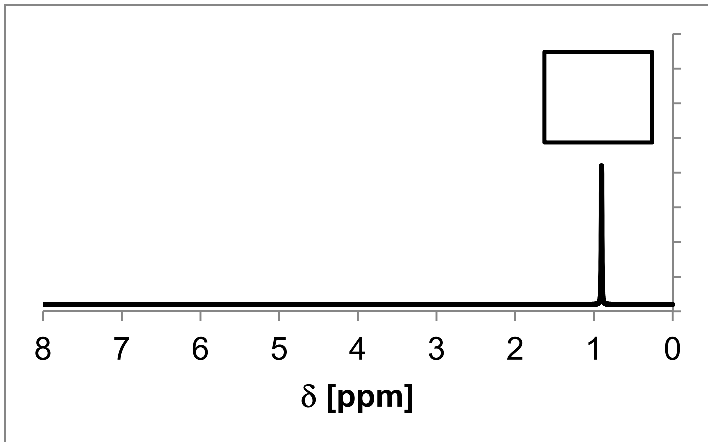
$$Fe(OH)_2(s) + 2\,e^- \rightarrow Fe(s) + 2\,OH^-(aq) \qquad \varepsilon_4° = -0.877\text{ V}$$

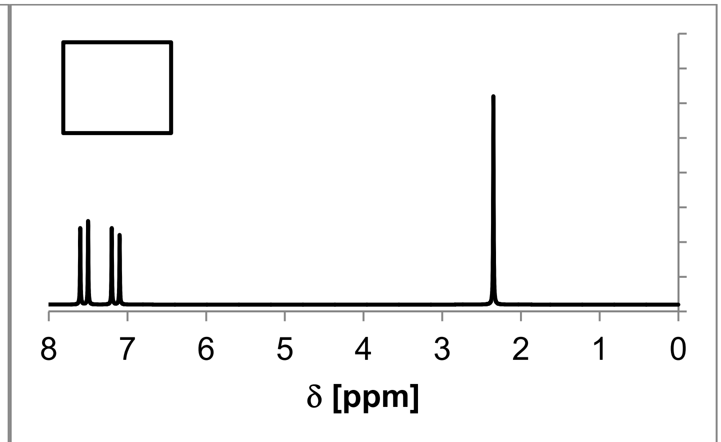
calculate the equilibrium constant (solubility product), K_{sp}, for the reaction:

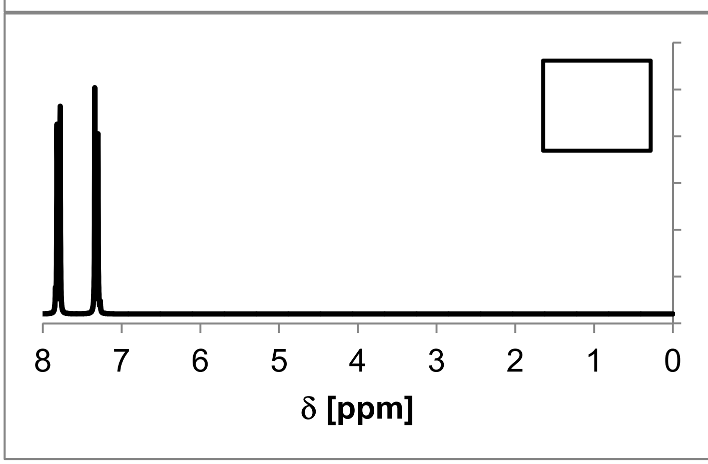
$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2\,OH^-(aq)$$

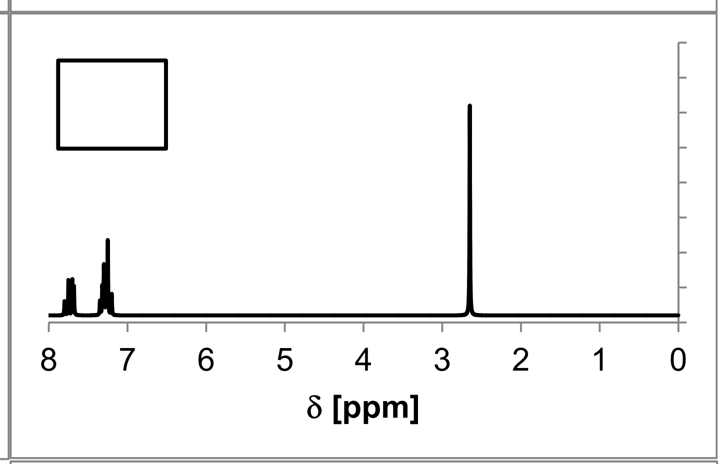
Part H: [6 marks] Assign the correct molecular formula (or structure) to each of the following [1]H NMR spectrum. Fill in the box using the appropriate number corresponding to a particular molecule, *e.g.*, 8. There is only one correct formula (or structure) for each NMR spectrum; two of the following molecules do not have a corresponding [1]H NMR spectrum.

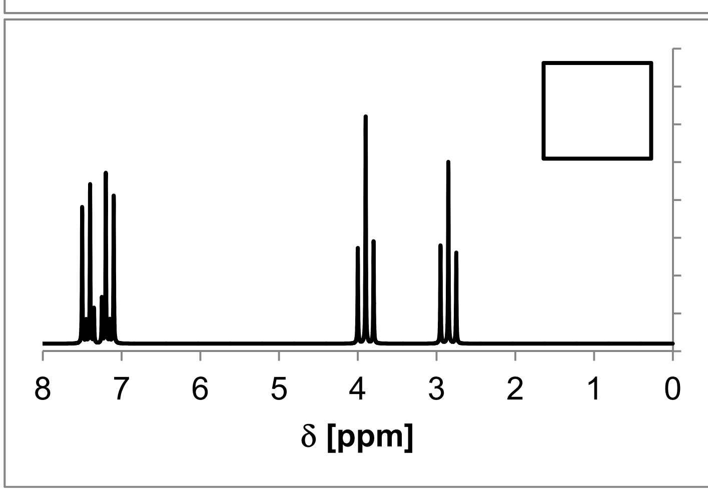


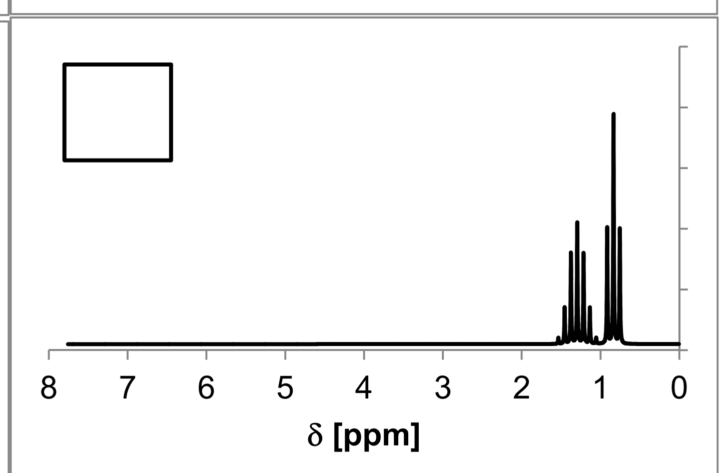




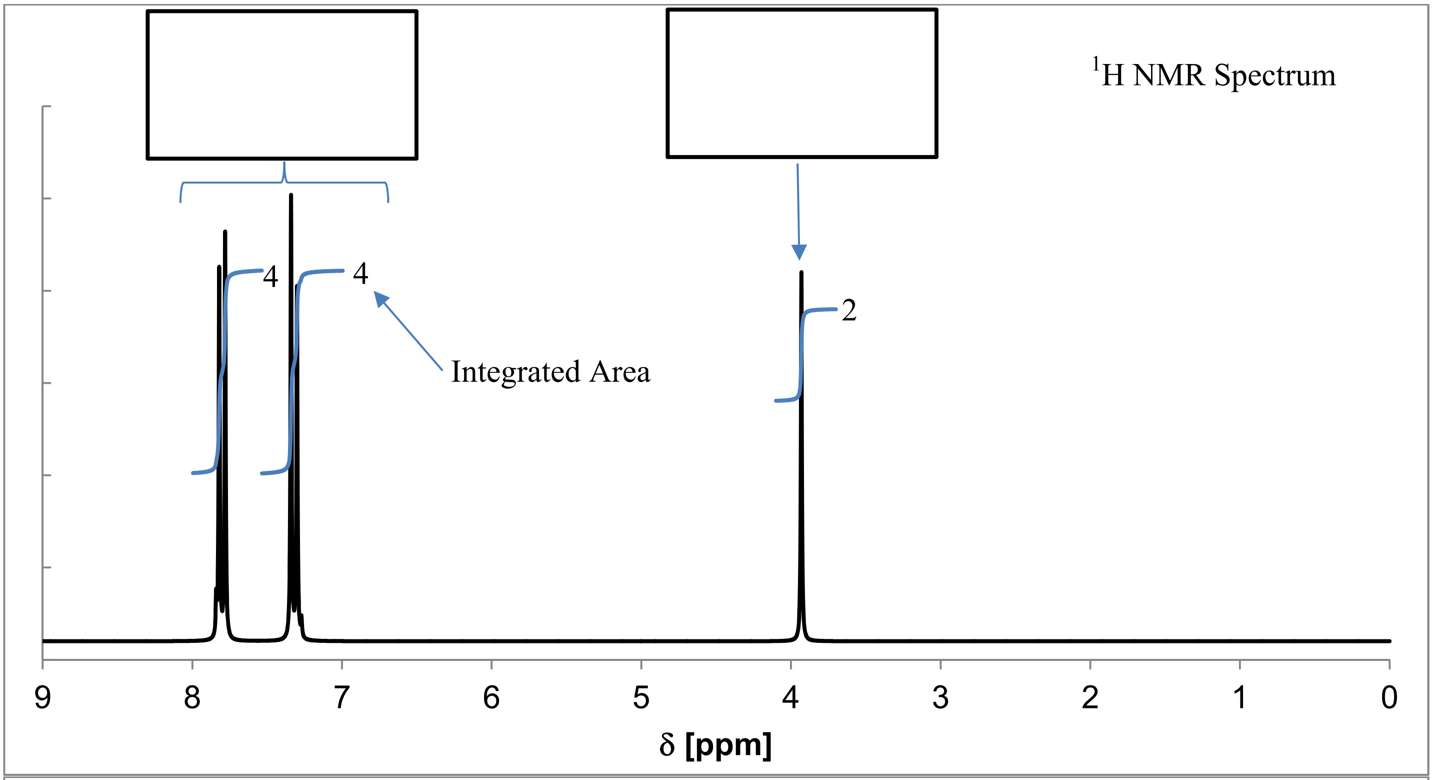


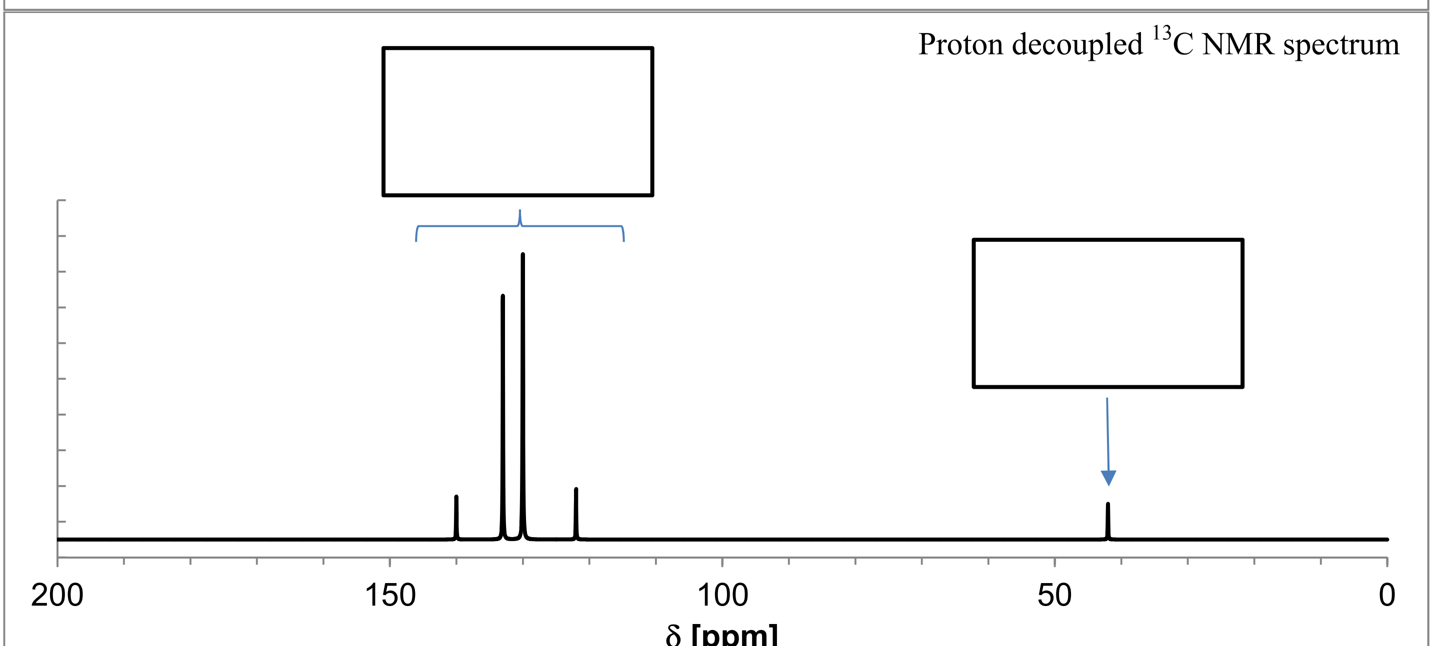


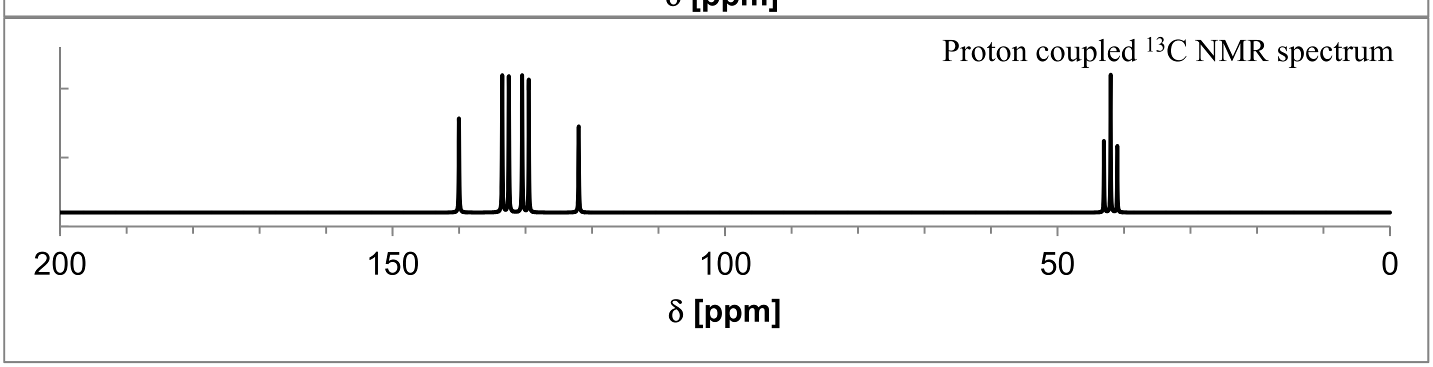


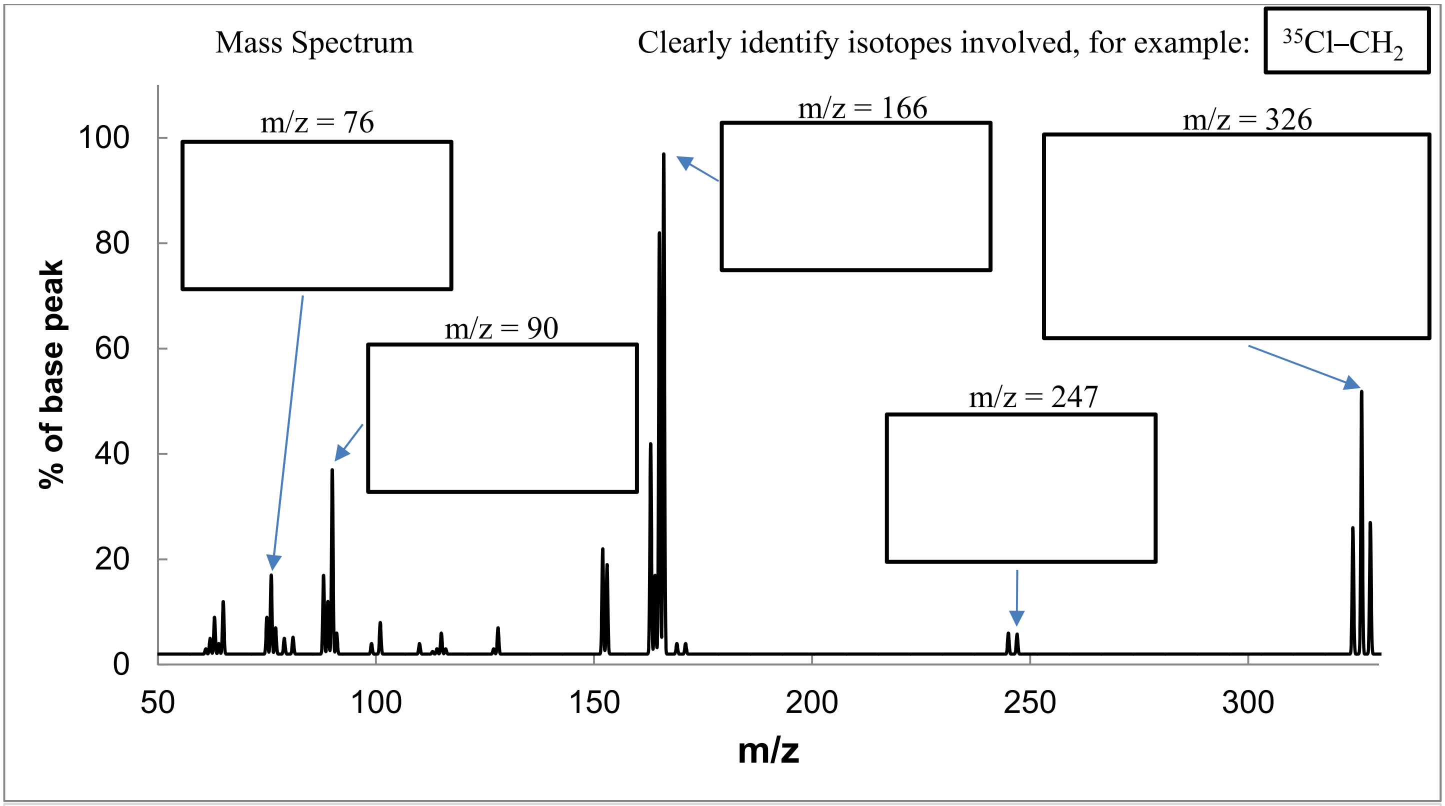


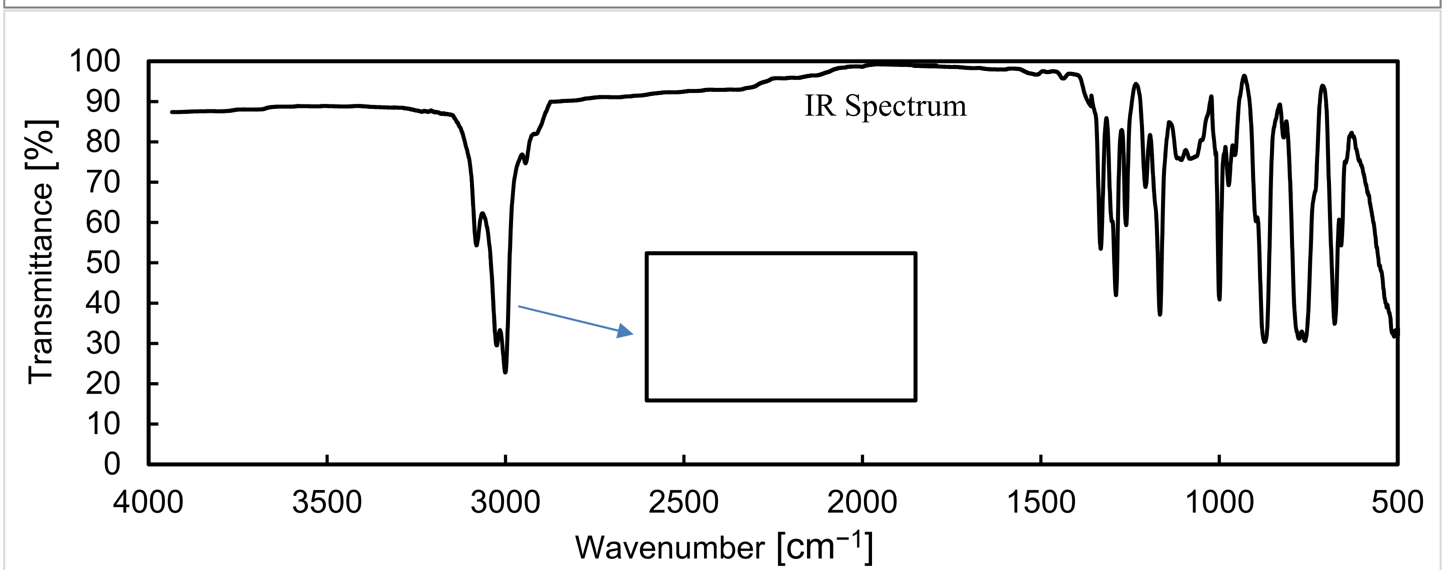
Part I: [12 marks] The following spectra were collected for a compound of formula $C_{13}H_{10}Br_2$. Fill the boxes in each spectrum to show which chemical moiety (*e.g.*, $–CH_3$, $–CH_2–$, *etc.*) gives rise to the peaks indicated by bracket or arrow. Draw the structure of the compound in the big empty box on the next page.



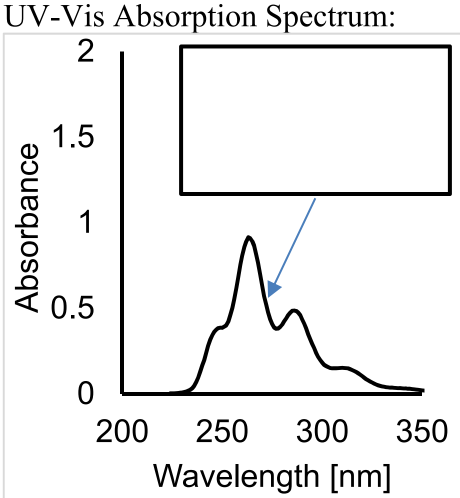








UV-Vis Absorption Spectrum:



Draw the structure of the molecule in the box:

Equations and Constants

(note: conditions for applying equations are **not** specified)

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$
$k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$
$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$
$F = 96485 \text{ C mol}^{-1}$
$0\ °\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 101325 \text{ Pa}$
$1 \text{ L} = 0.001 \text{ m}^3$
$1 \text{ L atm} = 101.325 \text{ J}$

$$PV = nRT$$
$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$
$$\Delta U = U_2 - U_1 = q + w$$
$$dw = -P_{ex} dV$$
$$w = -P_{ex}(V_2 - V_1)$$
$$w = -nRT \ln\left(\frac{V_2}{V_1}\right)$$
$$dq = C \cdot dT$$
$$C_V = nC_{V,m} = \frac{dq_V}{dT}$$
$$\Delta U = q_V = \int_{T_1}^{T_2} nC_{V,m} dT = \int_{T_1}^{T_2} C_V dT$$
$$H = U + PV$$
$$C_P = nC_{P,m} = \frac{dq_P}{dT}$$
$$\Delta H = q_P = \int_{T_1}^{T_2} nC_{P,m} dT = \int_{T_1}^{T_2} C_P dT$$
$$\Delta H^0_{rxn} = \sum_i \nu_i \Delta H^0_{m,i}(\text{products}) - \sum_j \nu_j \Delta H^0_{m,j}(\text{reatants})$$
$$C_{V,m} = \frac{3}{2}R, \quad C_{P,m} = \frac{5}{2}R$$

$$dS = dq_{rev}/T$$
$$\Delta S = S_2 - S_1 = \int_{\text{state 1}}^{\text{state 2}} \frac{dq_{rev}}{T}$$
$$(\Delta S)_{T,P} = \Delta H / T$$
$$(\Delta S)_T = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right)$$
$$(\Delta S)_V = nC_{V,m}\ln\left(\frac{T_2}{T_1}\right)$$
$$(\Delta S)_P = nC_{P,m}\ln\left(\frac{T_2}{T_1}\right)$$
$$\Delta S = nC_{V,m}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$
$$\Delta S = nC_{P,m}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)$$
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$
$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H^0_{vap,m}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0_{rxn}}{(1\text{ mol}) \cdot R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$\text{F} = \text{C} - \text{P} + 2$$
$$G = H - TS$$
$$\Delta G_{T,P} = -T \cdot \Delta S_{univ}$$
$$\Delta G_{rxn} = \Delta G^0_{rxn} + (1\text{ mol}) \cdot RT\ln Q$$
$$\Delta G^0_{rxn} = -(1\text{ mol}) \cdot RT\ln K$$
$$\Delta G_{rxn} = -nF\varepsilon, \quad \Delta G^0_{rxn} = -nF\varepsilon^0$$
$$\varepsilon = \varepsilon^0 - \frac{(1\text{ mol}) \cdot RT}{nF}\ln Q$$

$$\Delta T_b = T_{b,mix} - T_{b,pure} \approx K_b b_B$$
$$\Delta T_f = T_{f,mix} - T_{f,pure} \approx -K_f b_B$$
$$\Pi = c_B RT$$
$$\Delta\Pi = \Delta c \cdot RT$$
$$\varepsilon \approx \frac{-RT}{z_i F}\ln\left(\frac{[i]_R}{[i]_L}\right)$$
$$T = \frac{I}{I_0}$$
$$A = -\log_{10} T = lc\varepsilon$$
$$v = k[\text{A}]^a[\text{B}]^b[\text{C}]^c \cdots$$
$$a\text{A} \to \text{B}: \quad v = -\frac{1}{a}\frac{d[\text{A}]}{dt} = k[\text{A}]^n$$
$$a\text{A} \to \text{B}: \quad [\text{A}] = [\text{A}]_0 - akt, \quad t_{1/2} = \frac{[\text{A}]_0}{2ak}$$
$$a\text{A} \to \text{B}: \quad \ln\left(\frac{[\text{A}]}{[\text{A}]_0}\right) = -akt, \quad t_{1/2} = \frac{\ln 2}{ak}$$
$$a\text{A} \to \text{B}: \quad \frac{1}{[\text{A}]} - \frac{1}{[\text{A}]_0} = akt, \quad t_{1/2} = \frac{1}{ak[\text{A}]_0}$$
$$t = \frac{t_{1/2}}{\ln 0.5}\ln\left(\frac{[\text{A}]}{[\text{A}]_0}\right), \quad \frac{[\text{A}]}{[\text{A}]_0} = 0.5^{\frac{\text{time}}{\text{half-life}}}$$
$$K = \frac{k_1}{k_1'} \times \frac{k_2}{k_2'} \times \frac{k_3}{k_3'} \times \cdots$$
$$k = Ae^{\frac{-E_a}{RT}} = A\exp\left(\frac{-E_a}{RT}\right)$$
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$
$$v = \frac{[\text{S}] \cdot v_{max}}{[\text{S}] + K_M}, \quad v_{max} = k_b[\text{E}]_{tot}$$

Useful Spectroscopic Data

IR Modes of Vibrational Frequency	
Vibration	**ν (cm^{-1})**
C−C stretch,bend	700−1250
C−H stretch	2850−3100 (strong)
C−H bend	1340−1465
C=C stretch	1620−1680
C=O stretch	1600−1850 (strong)
C≡C stretch	2100−2260
C≡N stretch	2100−2300
O−H stretch	3590−3650 (strong)
C=N stretch	2215−2275
N−H stretch	3200−3500 (strong)
Hydrogen-bonds	3200−3570 (broad)

Selected Isotopes & Their Masses		
Isotope	**Natural Abundance**	**Mass**
^{1}H	99.98%	1.00783
^{12}C	98.9%	12.0000
^{13}C	1.1%	13.0034
^{14}N	99.6%	14.0031
^{16}O	99.8%	15.9949
^{19}F	100.0%	18.9984
^{35}Cl	75.8%	34.9689
^{37}Cl	24.2%	36.9659
^{79}Br	50.7%	78.9183
^{81}Br	49.3%	80.9163
^{127}I	100.0%	126.904

Common Fragments & Their Masses	
Fragment	**Mass**
CH_3	15
CH_2CH_3	29
HC(=O)	29
$HOCH_2$	31
CH_3C(=O)	43
HOC(=O)	45

UV-Visible Absorption Bands	
Chromophore	**λ_{max} (nm)**
C=O (carbonyl ketones, aldehydes, esters)	250−350 (weak)
CH=CH−CH=O (conjugated carbonyl)	200−300 (strong) and 300−400 (weak)
C=C (alkenes and conjugated alkenes)	160−340 (strong)
Benzene and derivatives	200−300 (moderate−strong)

^{1}H NMR Downfield Shifts from TMS	
Type of Proton ^{1}H	**Chemical Shift δ**
R**CH_3**	0.8 − 1.0
R**CH_2**R	1.2 − 1.4
R_3C**H**	1.4 − 1.7
R_2C=C(R)−**CH_3**	1.6 − 1.9
Ar**CH_3** (Ar is benzene ring)	2.2 − 2.5
R**CH_2**Cl	3.6 − 3.8
R**CH_2**Br	3.4 − 3.6
R**CH_2**I	3.1 − 3.3
RO**CH_2**R	3.3 − 3.9
R**CH_2**OH	3.3 − 4.0
RC(=O)**CH_3**	2.1 − 2.6
RC(=O)**H**	9.5 − 9.6
R_2C=**CH_2**	4.6 − 5.0
R_2C=C(R)**H**	5.2 − 5.7
Ar**H**	6.0 − 9.5
RC≡C**H**	2.5 − 3.1
RO**H**	0.5 − 6.0
RC(=O)O**H**	10 – 13
ArO**H**	4.5 − 7.7
R−N**H_2**	1.0 − 5.0

^{13}C NMR Chemical Shift Ranges	
Group	**^{13}C Shift δ**
TMS	0.0
−CH_3 (with only H or R at C_α or C_β)	0 – 30
−CH_2 (with only H or R at C_α or C_β)	20 − 45
−CH (with only H or R at C_α or C_β)	30 − 60
C quaternary (with only H or R at C_α or C_β)	30 − 50
O−CH_n (n = 0−3)	50 − 80
N−CH_n (n = 0−3)	15 − 70
C≡C	75 − 95
C=C	105 − 145
C(aromatic)	110 − 155
C(heteroaromatic)	105 − 165
−C≡N	115 − 125
C=O (acids, esters, amides)	155 − 185
C=O (aldehydes, ketones)	185 – 225

This final exam consists of **16** consecutively numbered pages including **two formula sheets at the very end**. Please check that your paper is complete before starting work. **You may peel off the last two pages of formula sheets.** All work must be shown on the first **14** pages in this booklet. Only the work written on the first **14** pages will be marked; anything written on the last two pages of formula sheets will be discarded and not be marked at all.

Family Name: ______________________ First Name: ______________________
(print, surname first)

Student Number: ______________________ Signature: ______________________

University of British Columbia
CHEM 205 Final Examination
11 April 2017, 3:30−6:00 PM

Time: 2 hours 30 minutes
Answer all questions
ALL CALCULATORS ARE PERMITTED

Answer Key

READ AND OBSERVE THE FOLLOWING EXAM RULES

1. Each examination candidate must be prepared to produce, upon the request of the invigilator or examiner, his or her UBCcard for identification.
2. Examination candidates are not permitted to ask questions of the examiners or invigilators, except in cases of supposed errors or ambiguities in examination questions, illegible or missing material, or the like.
3. No examination candidate shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination. Should the examination run forty five (45) minutes or less, no examination candidate shall be permitted to enter the examination room once the examination has begun.
4. Examination candidates must conduct themselves honestly and in accordance with established rules for a given examination, which will be articulated by the examiner or invigilator prior to the examination commencing. Should dishonest behaviour be observed by the examiner(s) or invigilator(s), pleas of accident or forgetfulness shall not be received.
5. Examination candidates suspected of any of the following, or any other similar practices, may be immediately dismissed from the examination by the examiner/invigilator, and may be subject to disciplinary action:
   (a) speaking or communicating with other examination candidates, unless otherwise authorized;
   (b) Purposely exposing written papers to the view of other examination candidates or imaging devices;
   (c) purposely viewing the written papers of other examination candidates;
   (d) using or having visible at the place of writing any books, papers or other memory aid devices other than those authorized by the examiner(s); and
   (e) using or operating electronic devices including but not limited to telephones, calculators, computers, or similar devices other than those authorized by the examiner(s) — (electronic devices other than those authorized by the examiner(s) must be completely powered down if present at the place of writing).
6. Examination candidates must not destroy or damage any examination material, must hand in all examination papers, and must not take any examination material from the examination room without permission of the examiner or invigilator.
7. Examination candidates must follow any additional examination rules or directions communicated by the examiner(s) or invigilator(s).

Question	Max	Mark
Part A	20	
Part B	12	
Part C	10	
Part D	11	
Part E	9	
Part F	10	
Part G	10	
Part H	6	
Part I	12	
Total	100	

Part A: [20 marks] Circle the **only one** correct answer for each of the following questions.

1. [1 mark] The energy difference between the reactants and the transition state is

1) $\Delta G_{reaction}$ 2) $\Delta H_{reaction}$ 3) $\Delta S_{reaction}$ 4) kinetic energy 5) activation energy

2. [1 mark] A cuvette filled with a green solution is placed in a spectrometer. It has been found that the intensity of the light passing through the sample is reduced by a factor of ten. Which of the following statements is true?

1) The absorbance of the green solution is 10%.
2) The absorbance of the green solution is 10.
3) The absorbance of the green solution is −1.
4) The transmittance of the green solution is 10.
5) The transmittance of the green solution is 10%.

3. [1 mark] The steps below represent a proposed mechanism for the catalyzed oxidation of CO by O_3:

Step 1: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Step 2: $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

Which of the following statements is true based on this mechanism?

1) The overall products are NO_2 and O_2.
2) The overall products are NO and CO_2.
3) The overall products are NO and O_2.
4) Either NO_2 or NO can be viewed as a catalyst.
5) Both NO_2 and NO are intermediates.

4. [1 mark] 0.01 M solutions of *t*-butanol in water and *n*-propanol in water are found to have the same osmotic pressure. This is because

1) *t*-butanol and *n*-propanol are about the same size.
2) both *t*-butanol and *n*-propanol are polar molecules and hence dissolve in water.
3) both *t*-butanol and *n*-propanol form hydrogen bonds with water.
4) at low concentration the osmotic pressure depends only on the molar concentration of the solute and not on its specific chemical nature.
5) *t*-butanol and *n*-propanol are both liquids at 25 °C and 1 atm.

5. [1 mark] An ideal gas undergoes an expansion from V_i to V_f ($V_f > V_i$) but $w = 0$ for the process. Which one of the following statements must be true?

1) The expansion was definitely reversible.
2) $\Delta U = 0$
3) The expansion was definitely irreversible.
4) $q = 0$
5) None of the above.

6. [1 mark] For the reaction, $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$, the rate law is $v = k[NO_2]^2$. At a fixed temperature, if the rate is measured immediately after a small amount of CO is added to a reaction mixture that is 0.10 M in NO_2 and 0.20 M in CO, which of the following statements is true?

1) Both k and the reaction rate v remain the same.

2) Both k and the reaction rate v increase.

3) Both k and the reaction rate v decrease.

4) Only k increases; the reaction rate v remains the same.

5) Only the reaction rate v increases; k remains the same.

7. [1 mark] When 4 moles of Ne are mixed with 7 moles of Ar while holding temperature and pressure constant, which one of the following equations is true?

1) $\Delta S_{sys} > 0$ 2) $\Delta S_{sys} = 0$ 3) $\Delta S_{sys} < 0$ 4) $\Delta S_{univ} = 0$ 5) None of the above

8. [1 mark] The resonance condition that applies to several types of spectroscopy can be written as $\Delta E = hv$. Indicate the region of the electromagnetic spectrum used for NMR spectroscopy.

1) the infrared region.

2) the ultraviolet-visible region.

3) the radio frequency region.

4) the microwave region.

5) the gamma ray region.

9. [1 mark] A sample of gallium metal is sealed inside a well-insultated, rigid container. The temperature inside the container is at the melting point of gallium metal. What can be said about the energy and the entropy of the system after equilibrium has been established? Assume the insulation and rigidity prevents any energy exchange with the surroundings.

1) The total energy and the total entropy both increase.

2) The total energy and the total entropy both decrease.

3) The total energy and the total entropy both remain constant.

4) The total energy is constant; the total entropy decreases.

5) The total energy is constant; the total entropy increases.

10. [1 mark] Given the following two reactions:

$$2\,M(s) + 3\,Zn^{2+}(aq) \rightarrow 2\,M^{3+}(aq) + 3\,Zn(s), \qquad \varepsilon_1° = 0.90\text{ V}$$

$$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s), \qquad \varepsilon_2° = -0.76\text{ V}$$

determine the standard reduction potential for the half-reaction: $M^{3+}(aq) + 3\,e^- \rightarrow M(s)$.

1) 0.90 V 2) −1.66 V 3) 1.66 V 4) −0.62 V 5) 0.14 V

11. [1 mark] For the overall reaction, $H_2O_2(aq) + 2\,Fe^{2+}(aq) + 2\,H^{+}(aq) \rightarrow 2\,Fe^{3+}(aq) + 2\,H_2O(l)$, when the concentration of $H^{+}(aq)$ is doubled, there is no change in the reaction rate. This indicates that

1) H^{+} is a spectator ion.

2) the rate determining step does not involve H^{+}.

3) the reaction mechanism does not involve H^{+}.

4) H^{+} is a catalyst.

5) H^{+} is an intermediate.

12. [1 mark] The reaction, $2\,Fe^{2+}(aq) + Zn(s) \rightarrow 2\,Fe^{3+}(aq) + Zn^{2+}(aq)$, is used in an electrochemical cell. The voltage measured for the cell was not equal to the calculated $\varepsilon°$ for the cell. Which of the following can cause this discrepancy?

1) The anion in the anode compartment is chloride instead of intrate as in the cathode compartment.

2) One or more of the ion concentrations is not 1 M.

3) Both of the solutions are at 25 °C instead of 0 °C.

4) The solution in the salt bridge is Na_2SO_4 instead of KNO_3.

5) None of the above.

13. [1 mark] The Second Law of thermodynamics determines if a process will be spontaneous or not. Therefore, if $\Delta S_{univ} > 0$ for a particular chemical reaction, which one of the following statements must be true?

1) $\Delta G < 0$

2) The reaction will be very fast.

3) The reaction will be fast only at the start.

4) The reaction will occur in the direction we have written, but we do not know the rate.

5) The reaction will occur slowly in the reverse direction.

14. [1 mark] The molecule Br_2 is not IR active. This is because

1) the molecule is linear.

2) halogen gases are too reactive for spectroscopy to be done.

3) the molecule has no vibrational states.

4) Br_2 is a brownish-red liquid at room temperature.

5) the molecule does not have a dipole moment.

15. [1 mark] In principle, what is the maximum number of phases that can coexist in a mixture of *t*-butanol and water?

1) 0 2) 1 3) 2 4) 3 5) 4

16. [1 mark] Consider a Donnan equilibrium across a semipermeable membrane that allows passage of water and all ions except a protein Pr^-. If at equilibrium, the system has Pr^-, Ca^{2+}, and Cl^- on side1 and Ca^{2+} and Cl^- on side 2, which of the following equations is correct?

1) Side 1: $2[Ca^{2+}] - [Cl^-] - [Pr^-] = 0$

2) Side 1: $[Ca^{2+}] - 2[Cl^-] - [Pr^-] = 0$

3) Side 2: $[Ca^{2+}] = [Cl^-]^2$

4) $\{[Ca^{2+}]^2\ [Cl^-]\}_{side\ 1} = \{[Ca^{2+}]^2\ [Cl^-]\}_{side\ 2}$

5) $\{[Ca^{2+}]\ [Cl^-]^2\ [Pr^-]\}_{side\ 1} = \{[Ca^{2+}]\ [Cl^-]^2\}_{side\ 2}$

17. [1 mark] Which one of the following statements concerning a catalyst is true?

1) It participates in the reaction mechanism.

2) It changes the equilibrium concentration of the products.

3) It does not affect a reaction energy path.

4) It always decreases the rate for a reaction.

5) It always increases the activation energy for a reaction.

18. [1 mark] When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant concentration increases

1) the average kinetic energy of molecules increases.

2) the frequency of molecular collisions increases.

3) the rate constant increases.

4) the activation energy increases.

5) the order of reaction increases.

19. [1 mark] If one mole of liquid water undergoes an adiabatic cyclic process, which one of the following statements concerning the work done on the system is correct?

1) $w > 0$ 2) $w < 0$ 3) $w = 0$ 4) $w = (3/2)\cdot RT$ 5) None of the above

20. [1 mark] In a simple voltaic (galvanic) cell, which one of the following statements correctly describes the purpose of the the salt bridge?

1) It is not necessary in order for the cell to work.

2) It acts as a mechanism to allow mechanical mixing of the solutions.

3) It allows charge balance to be maintained in the cell.

4) It acts as a membrane to block the passage of all ions.

5) It drives free electrons from one half-cell to the other.

Part B: **[12 marks]** At the normal sublimation point of 300 K, the heat of sublimation of lauric acid (molecular mass 200.32 g/mol) is 135.0 kJ/mol. The molar heat capacities of the solid and gasous forms of lauric acid are $C_{p,m}$(solid) = 360.58 J K^{-1} mol^{-1} and $C_{p,m}$(gas) = 931.17 J K^{-1} mol^{-1}, respectively. Under 1 atm pressure, when a sample of 100.0 g solid lauric acid is brought to a temperature of 600 K, the sample immediately sublimates. Calculate the changes in enthalpy and entropy of this process in the sample.

At the normal sublimation point $T_{\text{sub}} = 300$ K, the phase change is reversible: $\Delta G^0_{\text{sub},m} = 0$

$$\Delta G^0_{\text{sub},m} = \Delta H^0_{\text{sub},m} - T_{\text{sub}} \cdot \Delta S^0_{\text{sub},m} = 0 \;\Rightarrow\; \Delta S^0_{\text{sub},m(300\text{K})} = \frac{\Delta H^0_{\text{sub},m}}{T_{\text{sub}}} = \frac{135.0\times 10^3}{300} = 450.0 \ \text{J/(K}\cdot\text{mol)}$$

$$n = \frac{100\text{ g}}{200.32\text{ g/mol}} = 0.4992 \ \text{mol} \;\Rightarrow\; \begin{cases} \Delta H^0_{\text{sub}(300\text{K})} = n\,\Delta H^0_{\text{sub},m(300\text{K})} = 67.3922 \ \text{kJ} \\ \Delta S^0_{\text{sub}(300\text{K})} = n\,\Delta S^0_{\text{sub},m(300\text{K})} = 224.6406 \ \text{J/K} \\ C_{p,\text{gas}} - C_{p,\text{solid}} = n\,(C_{p,m,\text{gas}} - C_{p,m,\text{solid}}) = 284.8385 \ \text{J/K} \end{cases}$$

$$\Delta H^0_{\text{sub}(600\text{K})} = n\,\Delta H^0_{\text{sub},m(300\text{K})} + \int_{300\text{K}}^{600\text{K}} n\,(C_{p,m,\text{gas}} - C_{p,m,\text{solid}})\,dT = 67.3922 + 284.8385\times 300\times 10^{-3} = 152.84 \ \text{kJ}$$

$$\Delta S^0_{\text{sub}(600\text{K})} = n\,\Delta S^0_{\text{sub},m(300\text{K})} + \int_{300\text{K}}^{600\text{K}} \frac{n\,(C_{p,m,\text{gas}} - C_{p,m,\text{solid}})}{T}dT = 224.6406 + 284.8385\times\ln\left(\frac{600}{300}\right) = 422.08 \ \text{J/K}$$

Alternatively,

$$\begin{cases} \text{Cooling of the solid:} \begin{cases} \Delta H^0_{\text{cooling,solid}} = \int_{600\text{K}}^{300\text{K}} nC_{p,m,\text{solid}}dT = 180.002\times(-300)\times 10^{-3} = -54.001 \ \text{kJ} \\ \Delta S^0_{\text{cooling,solid}} = \int_{600\text{K}}^{300\text{K}} \frac{nC_{p,m,\text{solid}}}{T}dT = 180.002\times\ln\left(\frac{300}{600}\right) = -124.768 \ \text{J/K} \end{cases} \\ \text{Heating of the gas:} \begin{cases} \Delta H^0_{\text{heating,gas}} = \int_{300\text{K}}^{600\text{K}} nC_{p,m,\text{gas}}dT = 464.841\times 300\times 10^{-3} = 139.452 \ \text{kJ} \\ \Delta S^0_{\text{heating,gas}} = \int_{300\text{K}}^{600\text{K}} \frac{nC_{p,m,\text{gas}}}{T}dT = 464.841\times\ln\left(\frac{600}{300}\right) = 322.203 \ \text{J/K} \end{cases} \\ \Delta H^0_{\text{sub}(600\text{K})} = \Delta H^0_{\text{cooling,solid}} + \Delta H^0_{\text{sub}(300\text{K})} + \Delta H^0_{\text{heating,gas}} = -54.001 + 67.392 + 139.452 = 152.84 \ \text{kJ} \\ \Delta S^0_{\text{sub}(600\text{K})} = \Delta S^0_{\text{cooling,solid}} + \Delta S^0_{\text{sub}(300\text{K})} + \Delta S^0_{\text{heating,gas}} = -124.768 + 224.641 + 322.203 = 422.08 \ \text{J/K} \end{cases}$$

Part C: [10 marks] One mole of a monatomic ideal gas ($C_{v,m} = 3R/2$) initially at 300 K undergoes an adiabatic expansion against a constant external pressure of 2 atm increasing its volume from 1 L to 2 L.

(a) [8 marks] Calculate w, q, ΔU, ΔH, ΔS, ΔS_{surr}, and the final temperature T_f of the gas for this process.

$$\text{For adiabatic process: } q = 0 \Rightarrow \Delta S_{\text{surr}} = \frac{-q}{T_{\text{surr}}} = 0$$

$$w = -P_{\text{ex}} \cdot \Delta V = -P_{\text{ex}}(V_2 - V_1) == -2\times(2-1) = -2 \text{ L}\cdot\text{atm } (-202.65 \text{ J})$$
$$\Delta U = q + w = w = -202.65 \text{ J } (-2 \text{ L}\cdot\text{atm})$$

$$\Delta U = nC_{v,m}\Delta T = \frac{3R}{2}(T_f - 300) \Rightarrow \begin{cases} \Delta T = T_f - 300 = -16.25 \text{ K} \\ T_f = 283.75 \text{ K } (10.6 \text{ °C}) \end{cases}$$

$$C_{p,m} = C_{v,m} + R = \frac{5R}{2}$$
$$\Delta H = nC_{p,m}\Delta T = \frac{5R}{2}\Delta T = -337.75 \text{ J } (-3.333 \text{ L}\cdot\text{atm})$$

$$\Delta S = nC_{v,m}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) = \frac{3R}{2}\ln\left(\frac{283.75}{300}\right) + R\ln\left(\frac{2}{1}\right) = 5.068 \text{ J/K}$$

Alternatively,

$$\begin{cases} \dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2} \Rightarrow \dfrac{P_1}{P_2} = \dfrac{V_2}{V_1}\dfrac{T_1}{T_2} = \dfrac{2}{1}\times\dfrac{300}{283.75} = \dfrac{600}{283.75} \\ \Delta S = nC_{p,m}\ln\left(\dfrac{T_2}{T_1}\right) + nR\ln\left(\dfrac{P_1}{P_2}\right) = \dfrac{5R}{2}\ln\left(\dfrac{283.75}{300}\right) + R\ln\left(\dfrac{600}{283.75}\right) = 5.068 \text{ J/K} \end{cases}$$

(b) [2 marks] Is this process spontaneous? (circle the **only one** correct answer below)
Explain your answer.

1) Yes	2) No	3) Not enough information to know the answer.

(Answer boxed: 1) Yes)

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} = 5.068 \text{ J/K} > 0$$

ΔG cannot be used here because it is not an isobaric, isothermal process.

Part D: [11 marks] Answer the following questions for the reaction occurring in aqueous, basic solution:

$$I^-(aq) + OCl^-(aq) \rightarrow OI^-(aq) + Cl^-(aq)$$

(a) [5 marks] The initial rate of the reaction was studied and was shown to depend on $[I^-]_0$, $[OCl^-]_0$, and $[OH^-]_0$. Based on the following available data, determine the rate law and the rate constant.

Experiment	$[I^-]_0$ (M)	$[OCl^-]_0$ (M)	$[OH^-]_0$ (M)	Initial Rate (M/s)
#1	2.0×10^{-3}	1.5×10^{-3}	1.00	$v_1 = 1.8\times10^{-4}$
#2	4.0×10^{-3}	1.5×10^{-3}	1.00	$v_2 = 3.6\times10^{-4}$
#3	2.0×10^{-3}	3.0×10^{-3}	2.00	$v_3 = 1.8\times10^{-4}$
#4	4.0×10^{-3}	3.0×10^{-3}	1.00	$v_4 = 7.2\times10^{-4}$

$$v = k[I^-]^a[OCl^-]^b[OH^-]^c \Rightarrow \left\{\begin{array}{l} \frac{v_2}{v_1} = 2^a = 2 \Rightarrow a = 1 \\ \frac{v_4}{v_2} = 2^b = 2 \Rightarrow b = 1 \\ \frac{v_3}{v_1} = 2^b \cdot 2^c = 1 \Rightarrow c = -1 \end{array}\right\} \Rightarrow v = k\frac{[I^-][OCl^-]}{[OH^-]}$$

$$v_1 = k\frac{(0.002\text{ M})\cdot(0.0015\text{ M})}{1\text{ M}} \Rightarrow k = \frac{(1.8\times10^{-4}\text{ M/s})\times(1\text{ M})}{(0.002\text{ M})\cdot(0.0015\text{ M})} = 60.0\text{ s}^{-1}\text{ (Hz)}$$

(b) [6 marks] This reaction has the following proposed mechanism with rate constants k_1, k_2, k_3, and k_4:

$$\left\{\begin{array}{lll} \text{Step 1:} & OCl^-(aq) + H_2O(l) \rightarrow HClO(aq) + OH^-(aq) & k_1 \\ \text{Step 2:} & HClO(aq) + OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l) & k_2 \\ \text{Step 3:} & I^-(aq) + HClO(aq) \rightarrow HIO(aq) + Cl^-(aq) & k_3 \\ \text{Step 4:} & HIO(aq) + OH^-(aq) \rightarrow OI^-(aq) + H_2O(l) & k_4 \end{array}\right.$$

Using the **steady state approximation** and treating H_2O concentration as a constant, derive the rate law expression for this reaction based on this mechanism.

$$v = -\frac{d[OCl^-]}{dt} = -\frac{d[I^-]}{dt} = \frac{d[Cl^-]}{dt}$$

SSA for intermediate HClO:

$$\frac{d[HOCl]}{dt} = \underbrace{k_1[OCl^-][H_2O]}_{v_1} - \underbrace{k_2[HClO][OH^-]}_{v_2} - \underbrace{k_3[HClO][I^-]}_{v_3} = 0 \Rightarrow \left\{\begin{array}{l} v_1 - v_2 - v_3 = 0 \Rightarrow v_1 - v_2 = v_3 \\ [HClO] = \frac{k_1[OCl^-][H_2O]}{k_2[OH^-] + k_3[I^-]} \end{array}\right.$$

$$v = -\frac{d[OCl^-]}{dt} = v_1 - v_2 = \left\{\begin{array}{l} k_1[OCl^-][H_2O] - k_2[HClO][OH^-] \\ = v_3 = k_3[HClO][I^-] \end{array}\right\} = \frac{k_1k_3[I^-][OCl^-][H_2O]}{k_2[OH^-] + k_3[I^-]}$$

Alternatively (more simply),

$$v = -\frac{d[I^-]}{dt} = \frac{d[Cl^-]}{dt} = v_3 = k_3[HClO][I^-] = \frac{k_1k_3[I^-][OCl^-][H_2O]}{k_2[OH^-] + k_3[I^-]}$$

To be consistent with the experiments, $k_2[OH^-] >> k_3[I^-]$ in the above derived rate law.

Part E: **[9 marks]** The enzyme catalase catalyzes the decomposition of hydrogen peroxide (H_2O_2), with an activation energy E_a = 8.4 kJ/mol. The following data are obtained regarding the rate of reaction as a function of substrate concentration:

$[H_2O_2]_0$ (M)	0.002	0.005
Initial Rate (M/s)	2.76×10^{-3}	6.00×10^{-3}

The concentration of catalase is 3.5×10^{-9} M. Use these data to answer the following questions.

(a) [6 marks] Determine the maximum reaction rate v_{max}, the Michaelis constant K_M, and the rate constant k_b for the final product formation step of this enzyme catalyzed reaction.

$$v = \frac{[S]\cdot v_{max}}{[S]+K_M} \Rightarrow \frac{v_{max}}{v} = 1+\frac{K_M}{[S]} \Rightarrow \frac{1+\frac{K_M}{[S]_1}}{1+\frac{K_M}{[S]_2}} = \frac{v_2}{v_1}$$

$$\left.\begin{cases}[S]_1 = 0.005\ \text{M}, & v_1 = 6.00\ \text{mM/s}\\ [S]_2 = 0.002\ \text{M}, & v_2 = 2.76\ \text{mM/s}\end{cases}\right\} \Rightarrow \frac{1+\frac{K_M}{0.005}}{1+\frac{K_M}{0.002}} = \frac{2.76}{6.00} \Rightarrow K_M = \begin{cases}0.018\ \text{M}\\ 1.80\times10^{-2}\ \text{M}\\ 18.0\ \text{mM}\end{cases}$$

$$\begin{cases}v_{max} = v_1\cdot\left(1+\frac{K_M}{[S]_1}\right) = 6.00\times10^{-3}\times\left(1+\frac{0.018}{0.005}\right) = 0.0276\ \text{M/s}\ (27.6\ \text{mM/s})\\ v_{max} = k_b[E]_{tot} \Rightarrow k_b = \frac{v_{max}}{[E]_{tot}} = \frac{0.0276\ \text{M/s}}{3.5\times10^{-9}\ \text{M}} = \begin{cases}7.89\times10^{6}\ \text{s}^{-1}\ \text{(Hz)}\\ 7.89\ \text{MHz}\end{cases}\end{cases}$$

(b) [3 marks] It has been found that the rate constant of this enzyme catalyzed reaction increases by a factor of 1.50 from 10 °C to a higher final temperature. Determine this final temperature.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\ln(1.50) = -\frac{-8.4\times10^3}{8.314}\left(\frac{1}{T_2}-\frac{1}{283.15}\right)$$

$$T_2 = 319.45\ \text{K}\ (46.3\,^\circ\text{C})$$

Part F: **[10 marks]** At 37 °C, a solution of aluminum acetate, $Al(CH_3COO)_3 = Al^{3+} + 3\,CH_3COO^-$, is separated by a semipermeable membrane. Outside the cell, a triple-charged protein ion (whose counterion is either Al^{3+} or CH_3COO^-) is also present. The membrane is selectively permeable to everything in the system except for the protein ion. The equilibrium concentrations of CH_3COO^- inside the cell and Al^{3+} outside the cell are 60.0 mM and 50.0 mM, respectively.

(a) [5 marks] Calculate the equilibrium concentrations of CH_3COO^- outside the cell and Al^{3+} inside the cell.

$$\begin{cases} \text{inside chage balance: } 3[Al^{3+}]_{in} = [CH_3COO^-]_{in} \\ [Al^{3+}]_{in} = \dfrac{[CH_3COO^-]_{in}}{3} = \dfrac{60}{3} = 20 \text{ mM} \end{cases}$$

$$\begin{cases} \text{Donnan equilibrium condition: } [Al^{3+}]_{in}[CH_3COO^-]_{in}^3 = [Al^{3+}]_{out}[CH_3COO^-]_{out}^3 \\ [CH_3COO^-]_{out} = [CH_3COO^-]_{in} \cdot \left(\dfrac{[Al^{3+}]_{in}}{[Al^{3+}]_{out}}\right)^{\frac{1}{3}} = 60 \times \left(\dfrac{20}{50}\right)^{\frac{1}{3}} = 44.21 \text{ mM} \end{cases}$$

(b) [1 mark] Is the protein ion positively or negatively charged? (circle the only one correct answer below)

1) Positively charged   **[2) Negatively charged]**   3) Charge neutral

(c) [2 marks] Calculate the equilibrium concentration of the protein ion outside the cell.

$$\begin{cases} \text{outside chage balance: } (\pm 3)[Pr^{3\pm}]_{out} + 3[Al^{3+}]_{out} - [CH_3COO^-]_{out} = 0 \\ \pm[Pr^{3\pm}]_{out} = \dfrac{[CH_3COO^-]_{out}}{3} - [Al^{3+}]_{out} = \dfrac{44.21}{3} - 50 = -35.26 \text{ mM} \\ \text{Protein ion is an anion, with } [Pr^{3-}]_{out} = 35.26 \text{ mM} \end{cases}$$

(d) [2 marks] Calculate the absolute value of the Donnan potential across the cell membrane after the equilibrium is reached.

$$\left.\begin{aligned} \varepsilon &= \frac{-RT}{-F}\ln\left(\frac{[CH_3COO^-]_{out}}{[CH_3COO^-]_{in}}\right) = \frac{-8.314 \times 310.15}{-96485}\ln\left(\frac{44.21}{60}\right) = -0.0082 \text{ V} \\ \varepsilon &= \frac{-RT}{3F}\ln\left(\frac{[Al^{3+}]_{out}}{[Al^{3+}]_{in}}\right) = \frac{-8.314 \times 310.15}{3 \times 96485}\ln\left(\frac{50}{20}\right) = -0.0082 \text{ V} \end{aligned}\right\} \Rightarrow |\varepsilon| = \begin{cases} 0.0082 \text{ V} \\ 8.163 \text{ mV} \end{cases}$$

Part G: [10 marks] We know the following standard reduction potentials at 298 K:

$Fe^{2+}(aq) + 2\,e^- \rightarrow Fe(s)$ $\qquad \varepsilon_1° = -0.440$ V

$Fe^{3+}(aq) + 3\,e^- \rightarrow Fe(s)$ $\qquad \varepsilon_2° = -0.0363$ V

(a) [3 marks] In the empty boxes below, write the overall cell reaction in the direction of spontaneous change and write out the actual reactions (*i.e.*, reduction and oxidation) occurring at the electrodes.

Anode (Oxidation)	$Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-$	$3 \times$ Oxidation, $n_{ox} = 6$
Cathode (Reduction)	$Fe^{3+}(aq) + 3\,e^- \rightarrow Fe(s)$	$2 \times$ Reduction, $n_{red} = 6$
Total Cell Reaction	$Fe(s) + 2\,Fe^{3+}(aq) \rightarrow 3\,Fe^{2+}(aq)$	But, $n_{cell} = 2$ only

(b) [3 marks] Calculate $\Delta G°$ and the standard cell potential $\varepsilon°$ for the total cell reaction.

$$\left.\begin{aligned} \Delta G^0_{ox} &= -n_{ox}F(-\varepsilon^0_1) = 6F\varepsilon^0_1 \\ \Delta G^0_{red} &= -n_{red}F\varepsilon^0_2 = -6F\varepsilon^0_2 \end{aligned}\right\} \Rightarrow \left\{\begin{aligned} \Delta G^0_{cell} &= \Delta G^0_{ox} + \Delta G^0_{red} = -6F(\varepsilon^0_2 - \varepsilon^0_1) \\ \Delta G^0_{cell} &= -n_{cell}F\varepsilon^0_{cell} = -2F\varepsilon^0_{cell} \end{aligned}\right\} \Rightarrow \varepsilon^0_{cell} = 3 \times (\varepsilon^0_2 - \varepsilon^0_1)$$

$$\varepsilon^0_{cell} = 3 \times (\varepsilon^0_2 - \varepsilon^0_1) = 3 \times [-0.0363 - (-0.440)] = 1.2111 \text{ V}$$

For the total cell, oxidation number changes tell $n_{cell} = 2$ only.

$$\Delta G^0 = -n_{cell}F\varepsilon^0_{cell} = -2 \times 96485 \times 1.2111 = -233.71 \text{ kJ } (-233706 \text{ J})$$

$$\text{Or: } \Delta G^0 = \Delta G^0_{ox} + \Delta G^0_{red} = -6F(\varepsilon^0_2 - \varepsilon^0_1) = -6 \times 96485 \times 0.4037 = -233.71 \text{ kJ } (-233706 \text{ J})$$

(c) [4 marks] Given the following half-cell reaction at 298 K for the low-insolubility base $Fe(OH)_2(s)$:

$Fe(OH)_2(s) + 2\,e^- \rightarrow Fe(s) + 2\,OH^-(aq)$ $\qquad \varepsilon_4° = -0.877$ V

calculate the equilibrium constant (solubility product), K_{sp}, for the reaction:

$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2\,OH^-(aq)$

$$\begin{cases} a: & Fe(OH)_2(s) + 2\,e^- \rightarrow Fe(s) + 2\,OH^-(aq), & \varepsilon^0_4, & \Delta G^0_a = -2F\varepsilon^0_4 \\ b: & Fe(s) \rightarrow Fe^{2+}(aq) + 2\,e^-, & -\varepsilon^0_1, & \Delta G^0_b = -2F(-\varepsilon^0_1) = 2F\varepsilon^0_1 \\ a+b: & Fe(OH)_2(s) \xleftrightarrow{K_{sp}} Fe^{2+}(aq) + 2\,OH^-(aq), & \varepsilon^0_3 = \varepsilon^0_4 - \varepsilon^0_1, & \Delta G^0_3 = \Delta G^0_a + \Delta G^0_b = 2F(\varepsilon^0_1 - \varepsilon^0_4) \end{cases}$$

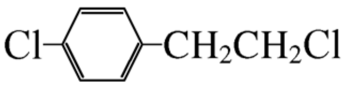
$$\varepsilon^0_3 = \varepsilon^0_4 - \varepsilon^0_1 = -0.877 - (-0.440) = -0.437 \text{ V}$$

$$\varepsilon^0_3 = \frac{(1\,\text{mol}) \cdot RT}{2F} \ln K_{sp} \Rightarrow \ln K_{sp} = \frac{2F\varepsilon^0_3}{(1\,\text{mol}) \cdot RT} = \frac{2 \times 96485 \times (-0.437)}{8.314 \times 298} = -34.0365 \Rightarrow K_{sp} = 1.65 \times 10^{-15}$$

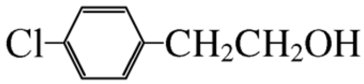
Alternatively,

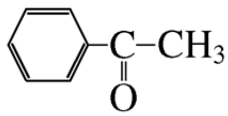
$$\left.\begin{aligned} \Delta G^0_3 &= \Delta G^0_a + \Delta G^0_b = 2F(\varepsilon^0_1 - \varepsilon^0_4) \\ \Delta G^0_3 &= -(1\,\text{mol}) \cdot RT \cdot \ln K_{sp} \end{aligned}\right\} \Rightarrow \ln K_{sp} = \frac{2F(\varepsilon^0_1 - \varepsilon^0_4)}{-(1\,\text{mol}) \cdot RT} = -34.0365 \Rightarrow K_{sp} = 1.65 \times 10^{-15}$$

Part H: [6 marks] Assign the correct molecular formula (or structure) to each of the following [1]H NMR spectrum. Fill in the box using the appropriate number corresponding to a particular molecule, *e.g.*, 8. There is only one correct formula (or structure) for each NMR spectrum; two of the following molecules do not have a corresponding [1]H NMR spectrum.

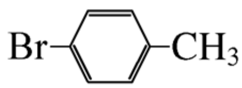
1) 

2) $CH_3CH_2CH_2CH_3$

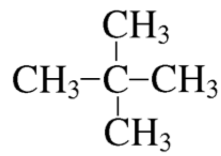
3) 

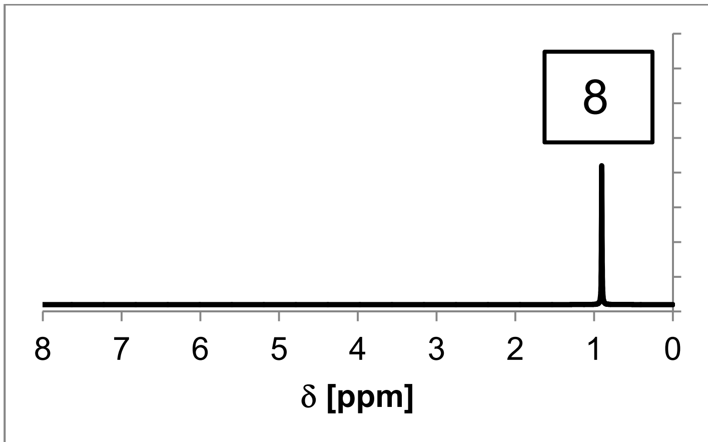
4) 

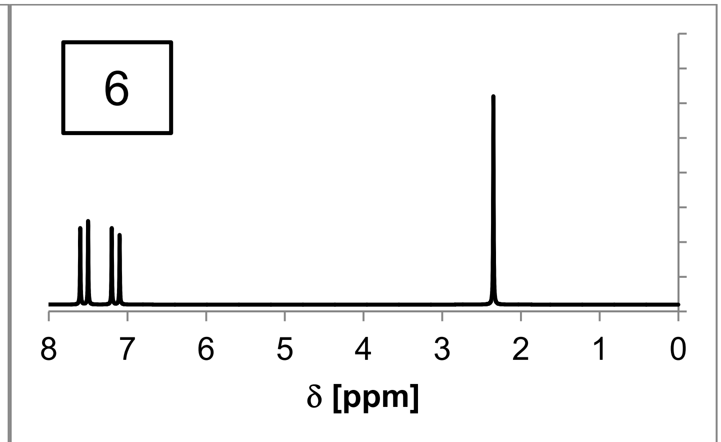
5) $CH_3CH_2CH_3$

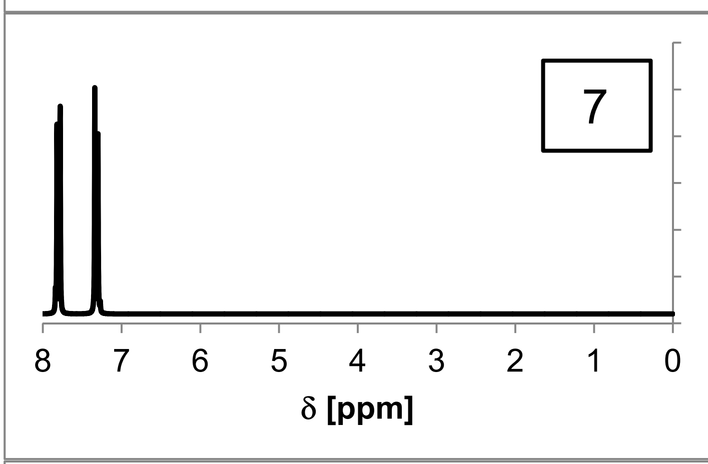
6) 

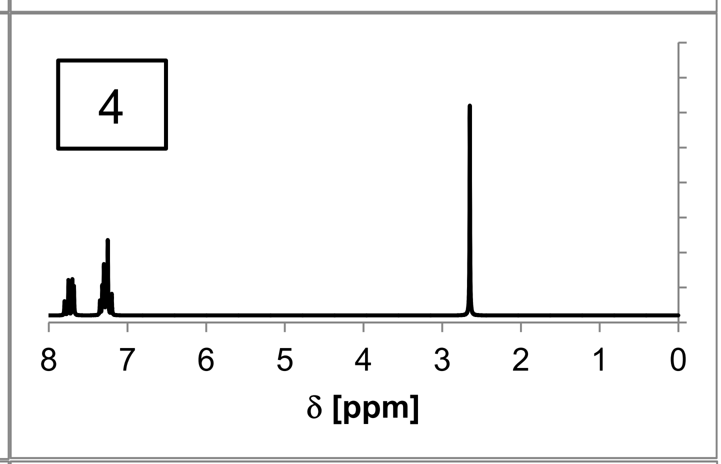
7) 

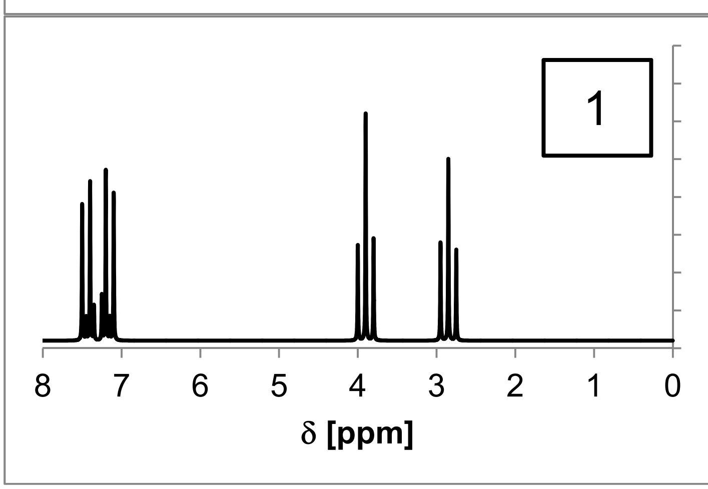
8) 

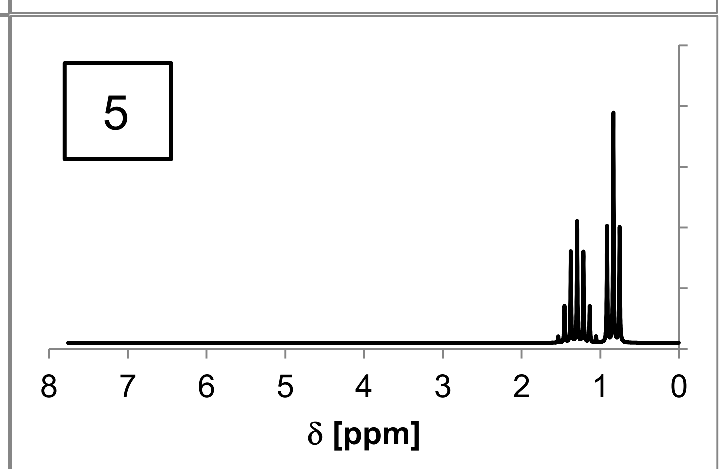




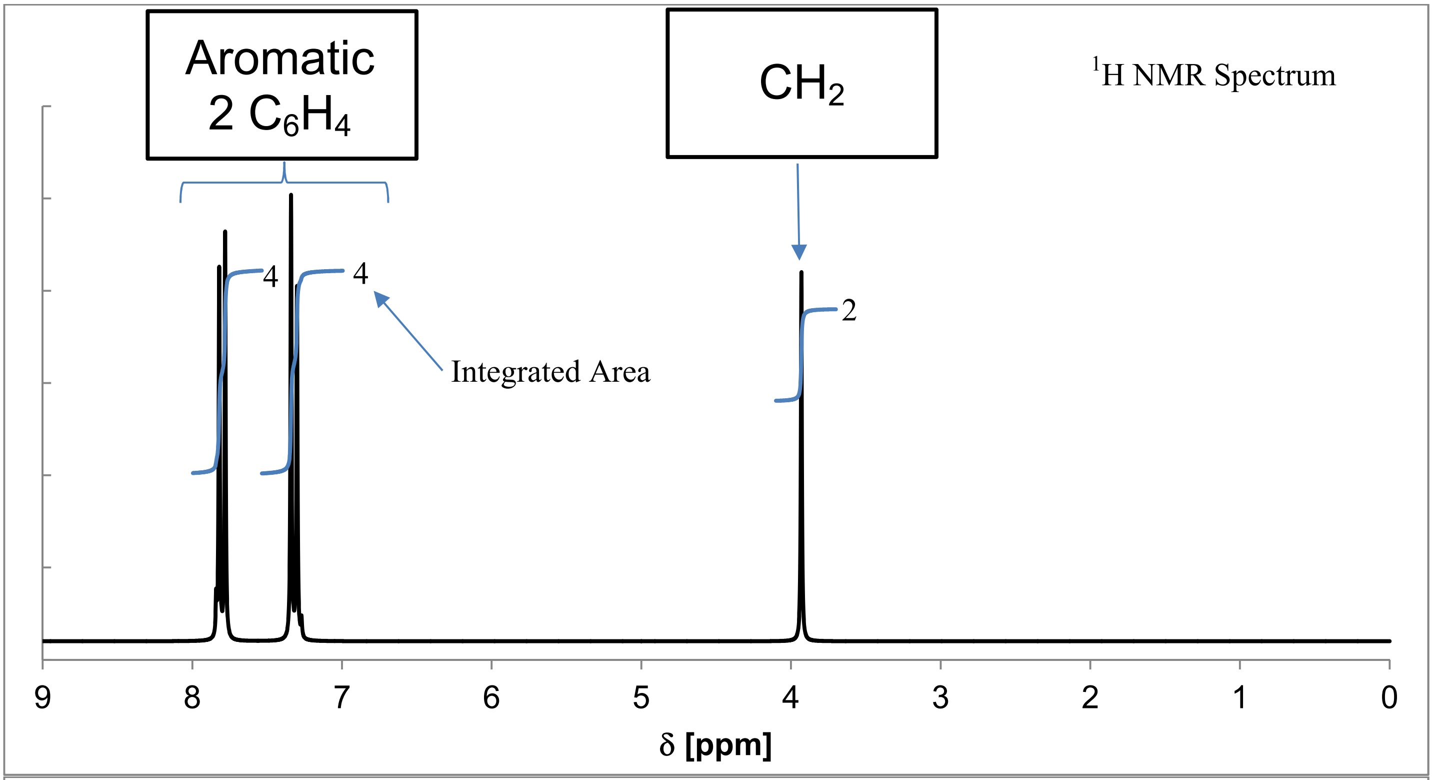


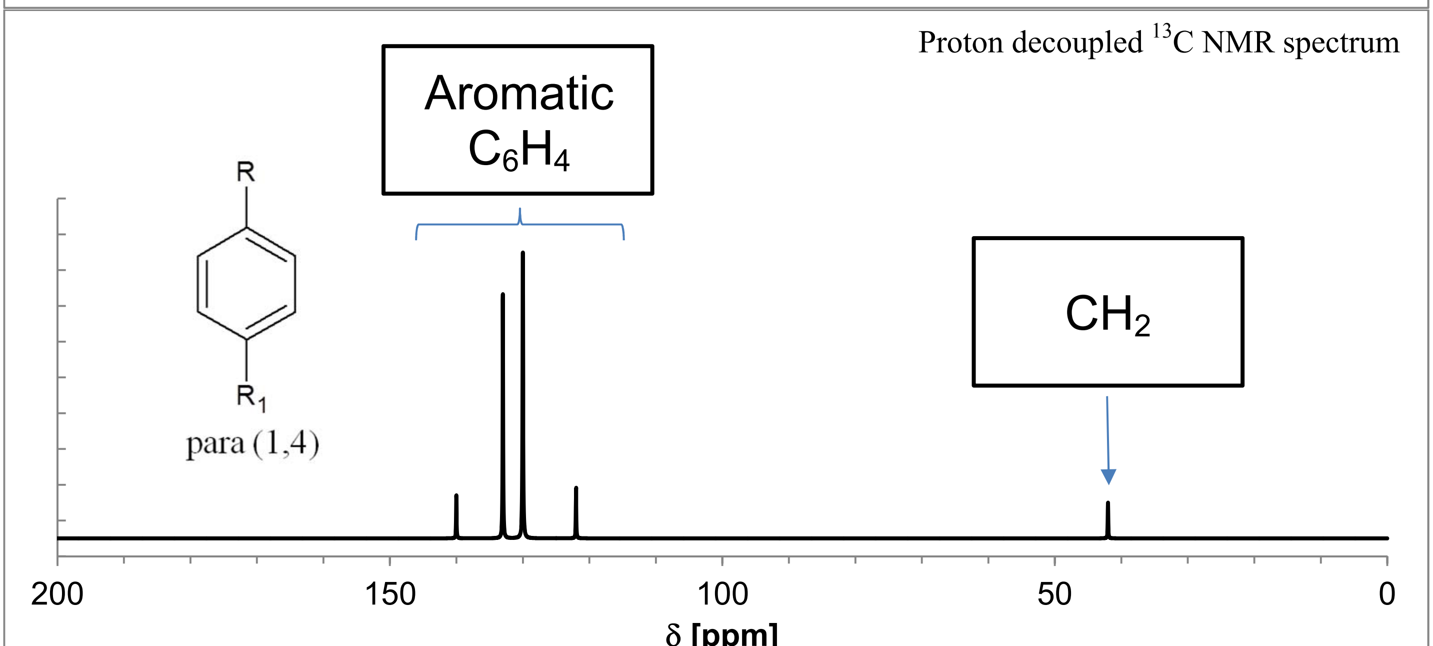


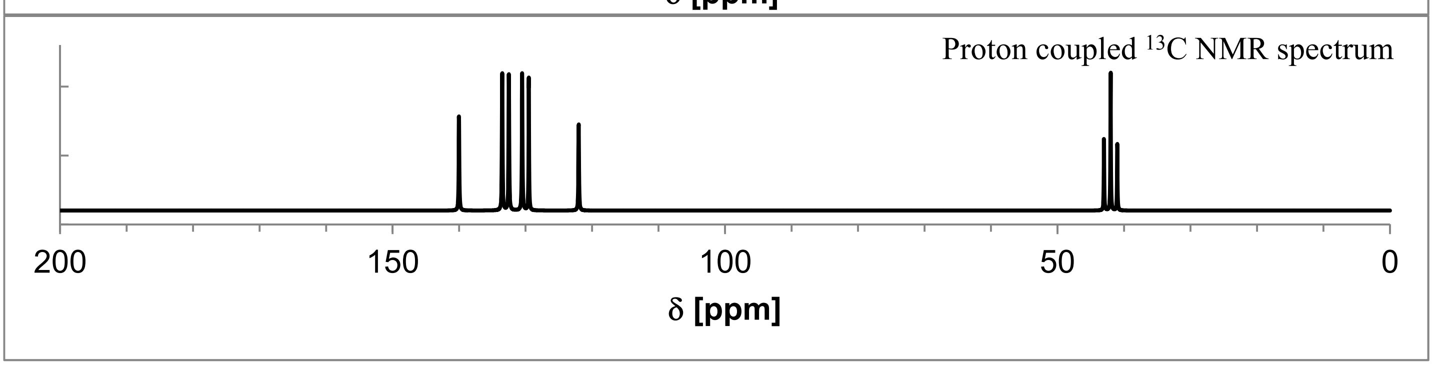


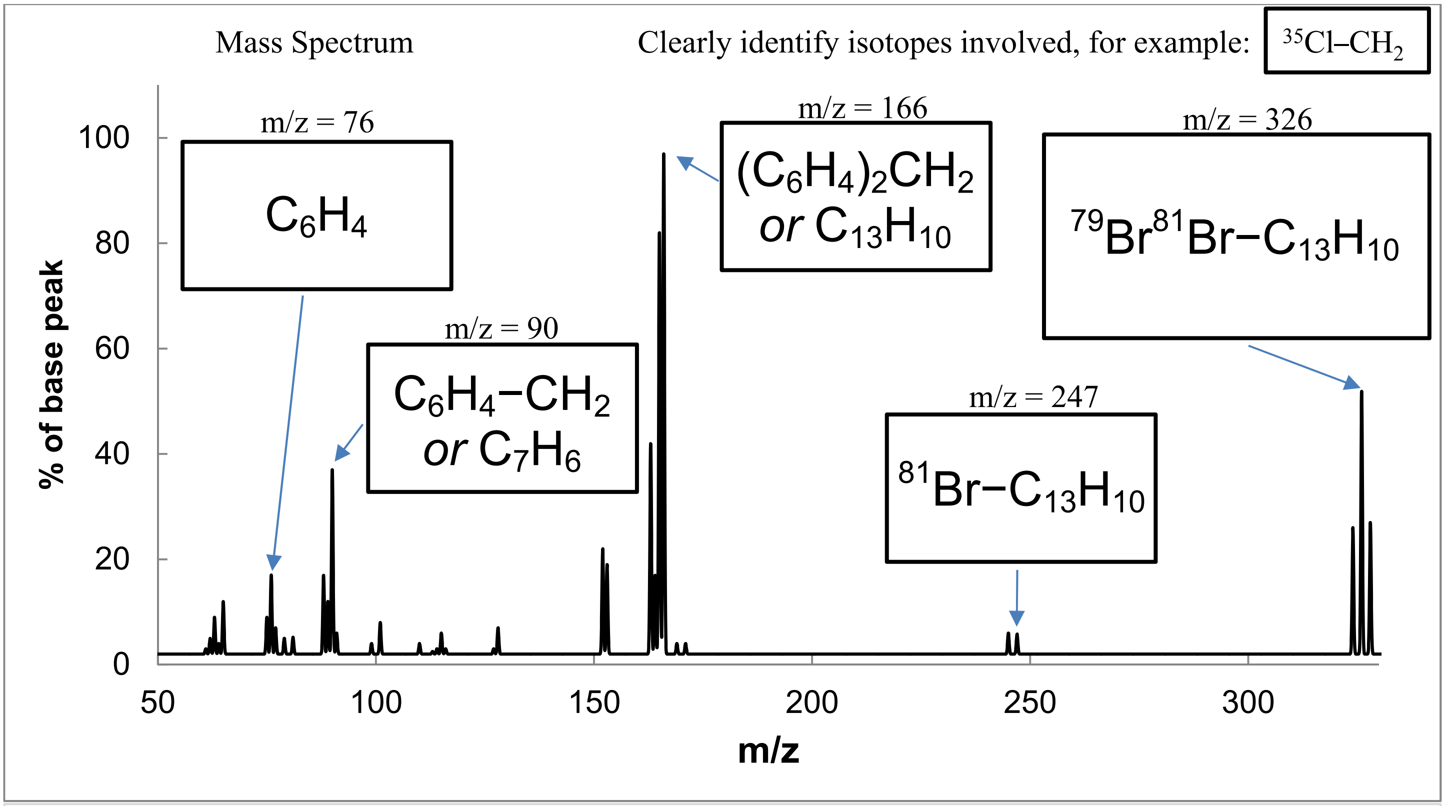


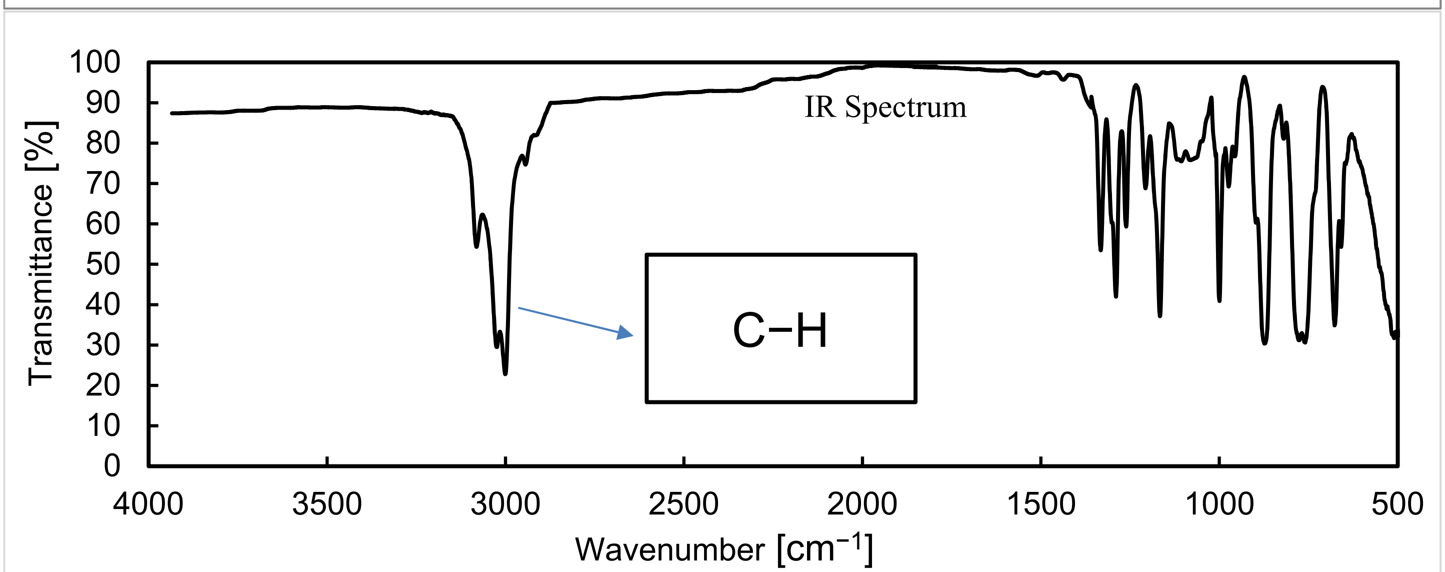
Part I: [12 marks] The following spectra were collected for a compound of formula $C_{13}H_{10}Br_2$. Fill the boxes in each spectrum to show which chemical moiety (*e.g.*, $–CH_3$, $–CH_2–$, *etc.*) gives rise to the peaks indicated by bracket or arrow. Draw the structure of the compound in the big empty box on the next page.



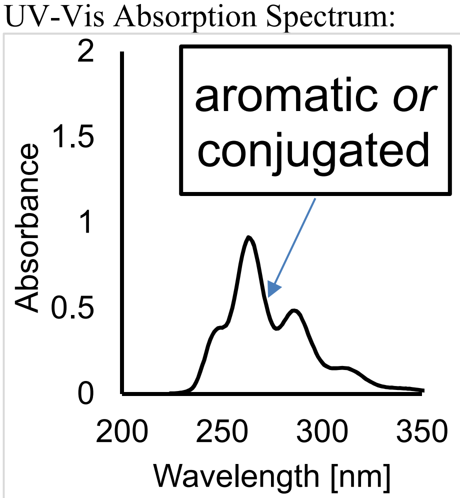








UV-Vis Absorption Spectrum:



Draw the structure of the molecule in the box: