This final exam consists of **17** 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 **15** pages in this booklet. Only the work written on the first **15** 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
13 April 2019, 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	10	
Part C	8	
Part D	6	
Part E	4	
Part F	2	
Part G	12	
Part H	11	
Part I	10	
Part J	6	
Part K	11	
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] If the order of a chemical reaction (in the rate law) is −1, the units of the rate constant is

1) $\mathrm{mol^2\ L^{-2}\ s^{-1}}$ 2) $\mathrm{mol\ L^{-1}\ s^{-1}}$ 3) $\mathrm{L\ mol^{-1}\ s^{-1}}$ 4) $\mathrm{L^2\ mol^{-2}\ s^{-1}}$ 5) $\mathrm{s^{-1}}$

2. [1 mark] A sample of an ideal gas, contained within a closed vessel, undergoes some process starting from 1 atm and 2 L and arriving at 4 atm and 0.5 L. Which one of the following statements is always true?

1) During the entire process, T is a constant.

2) During the entire process, U is a constant.

3) During the entire process, H is a constant.

4) $\Delta H = H_{\text{final}} - H_{\text{initial}} = 0$.

5) $q > 0$.

3. [1 mark] A peak in an NMR spectrum of a molecule directly represents

1) a nuclear spin state of the molecule.

2) an electron spin transition of the molecule.

3) a vibrational transition of the molecule.

4) a rotational transition of the molecule.

5) none of the above.

4. [1 mark] Elementary termolecular reactions are normally very slow because

1) elementary termolecular reactions take many steps to finish.

2) a termolecular reaction is made of a unimolecular reaction and a dimolecular reaction.

3) the more molecules collide at the same time, the faster the elementary reaction will proceed.

4) the probability for three molecules to collide at the same time is low.

5) none of the above.

5. [1 mark] A dye solution of concentration 0.1 mol/L was measured to have a transmittance of 0.1 at 550 nm. The path length of the light passing through the solution was 1 cm. What is the molar extinction coefficient (molar absorptivity) of the dye molecule?

1) $1\ \mathrm{L^{-1}\ mol^{-1}\ cm^{-1}}$ 2) $10\ \mathrm{m^3\ mol^{-1}\ cm^{-1}}$ 3) $1\ \mathrm{L\ mol^{-1}\ m^{-1}}$ 4) $10\ \mathrm{L\ mol^{-1}\ cm^{-1}}$ 5) $10\ \mathrm{L^{-1}\ mol^{-1}\ cm^{-1}}$

6. [1 mark] For a given chemical reaction happening at a fixed temperature,

1) a catalyst can only change the rate constants.

2) a catalyst can only change the forward reaction's rate constant.

3) a catalyst can only change the equilibrium constant.

4) a catalyst can change both the rate constant and the equilibrium constant.

5) a catalyst can change neither the rate constant nor the equilibrium constant.

7. [1 mark] The following statement for chemical equilibrium applies to the equation: $\Delta G = \Delta G^\circ + RT\ln Q$

1) At equilibrium, $Q = 0$ and $\Delta G = 0$.

2) At equilibrium, $\Delta G^\circ = 0$ and $Q = K$.

3) Because $\Delta G^\circ = -RT\ln K$, ΔG° is a measure of the Gibbs energy difference between products and reactants at equilibrium.

4) At equilibrium, $\Delta G^\circ = \Delta G$ and $Q = 1$.

5) None of the above.

8. [1 mark] Using IR spectroscopy, we **cannot** observe the vibrational modes in

1) CO 2) H_2O 3) Xe 4) CO_2 5) CH_4

9. [1 mark] To calculate the expansion work for a process,

1) the formula $w = -P_{ex}(V_2 - V_1)$ always works under all conditions.

2) the formula $dw = -P_{ex}\,dV$ can only be used for irreversible processes.

3) the formula $dw = -P_{ex}\,dV$ always works under all conditions.

4) the formula $w = -nRT\ln(V_2/V_1)$ always works for any isothermal reversible process.

5) None of the above is applicable.

10. [1 mark] Upon reaching equilibrium during an osmosis process across a semipermeable membrane of a biological cell between fresh water (outside the cell) at **2 atm** pressure and a salt solution (inside the cell), what is the pressure P exerted on the side of the salt solution?

1) $P = 1$ atm

2) $P = 2$ atm

3) $P = \Pi$ (the osmotic pressure)

4) $P = \Pi + 2$ atm

5) $P = \Pi + 1$ atm

11. [1 mark] If a **proposed** chemical reaction is exothermic and results in a decrease in the entropy of the system, this chemical reaction:

1) will proceed forward spontaneously.
2) will proceed backward spontaneously.
3) will be in equilibrium.
4) will not react at all.
5) The information given is insufficient to determine the spontaneity of the reaction.

12. [1 mark] Which one of the following statements about electromagnetic radiation is correct?

1) Infrared light is in red color.
2) Ultraviolet light has extremely violet color.
3) X-ray is in black and white.
4) Visible light is always white unless it is in the rainbows.
5) None of the above.

13. [1 mark] In a rundown AA alkaline battery just taken out of an old toy,

1) no more energy can be supplied because the battery is no longer in equilibrium condition.
2) no more energy can be supplied because all reactants are used up.
3) no more energy can be supplied because there are no electrons left in the battery.
4) no more energy can be supplied because the reactants and products of the electrochemical reaction is approaching equilibrium.
5) the ΔG of the system is negative.

14. [1 mark] At the same temperature and pressure, the equilibrium constant of the first reaction $2\,A(g) + 2\,B(g) \rightleftharpoons D(g)$ is K_1, and the equilibrium constant of the second reaction $\frac{1}{2}\,D(g) \rightleftharpoons A(g) + B(g)$ is K_2, which one of the following statements is correct?

1) $K_2 = -K_1$ 2) $K_2 = K_1$ 3) $K_2 = (K_1)^{0.5}$ 4) $K_2 = (K_1)^{-0.5}$ 5) None of the above

15. [1 mark] For a unimolecular dissociation reaction: $A_2 \rightarrow 2\,A$, the change of the amount of the product per unit time, C_A, and the average rate of this reaction, v_{mean}, are related according to

1) $C_A = v_{mean}$ 2) $2\,C_A = v_{mean}$ 3) $C_A = 2\,v_{mean}$ 4) $2\,C_A = -v_{mean}$ 5) $C_A = -2\,v_{mean}$

16. [1 mark] The decomposition of O_3 in the upper atmosphere, $2O_3(g) \rightarrow 3O_2(g)$, **involves** the following two elementary reactions in the mechanism:

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$$

$$O_3 + ClO\cdot \rightarrow Cl\cdot + 2\,O_2$$

Which one of the following statements concerning the above reaction is true?

1) Neither ClO· nor Cl· is an intermediate or a catalyst.

2) ClO· is an intermediate; Cl· is a catalyst.

3) ClO· is a catalyst; Cl· is an intermediate.

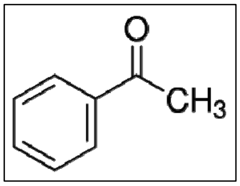
4) Both ClO· and Cl· are catalysts.

5) We cannot tell from the given information whether a catalyst is present.

17. [1 mark] Two moles of a monatomic ideal gas is confined within a two-dimensional plane at constant T. What is the internal energy of this system according to the Equipartition Principle?

1) RT
2) $(1/2)\cdot RT$
3) $2\,RT$
4) $(3/2)\cdot RT$
5) $3\,RT$

18. [1 mark] Which one of the following is **not** true regarding the spectra of acetophenone $C_6H_5{-}CO{-}CH_3$:



1) in the ^{1}H NMR, the CH_3 group will appear as a singlet.

2) the ^{13}C NMR will have a singlet at approximately 200 ppm.

3) the IR spectrum will display a significant absorption at about 2400 cm^{-1}.

4) in the ^{1}H NMR, the CH_3 group will absorb at approximately $\delta = 2.2$ ppm.

5) in the mass spectrum, a significant peak will occur at m/z = 43.

19. [1 mark] The maximum number of coexisting phases for a mixture of toluene, benzene, and acetone is

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

20. [1 mark] After adding some table salt to a cup of pure water, how do the boiling point and freezing point of the salt solution change with respect to those of pure water?

1) Both the boiling point and freezing point of the salt solution stay the same.

2) Both the boiling point and freezing point of the salt solution decrease.

3) Both the boiling point and freezing point of the salt solution increase.

4) The boiling point of the salt solution increases whereas the freezing point of the salt solution decreases.

5) The boiling point of the salt solution decreases whereas the freezing point of the salt solution increases

Part B: **[10 marks]** Three moles of an ideal gas undergoes an isothermal process at T = 25 °C, from an initial pressure of 1 atm to a final pressure of 3 atm. Throughout the entire process, the external pressure on the gas is maintained equal to the final pressure of the gas, and the temperature of the surroundings is also kept the same as the temperature of the system. (**Note**: 0 °C = 273.15 K)

(a) [5 marks] Calculate w, q, ΔU, and ΔH for this process.

(b) [4 marks] Calculate ΔS_{system} and ΔG for this process.

(c) [1 mark] Is the process spontaneous? (circle the **only one** correct answer below)

1) Yes 2) No 3) Can be either spontaneous or nonsponstaneous

Part C: [8 marks] The following vapor pressures were measured for SO_2 gas in equilibrium with liquid SO_2:

T (°C)	−46.9	6.3
P (kPa)	1.333	20.270

(a) [6 marks] Calculate ΔG, ΔH, and ΔS for the vaporization of SO_2 at 6.3 °C and 20.270 kPa. (**Note**: 0 °C = 273.15 K)

(b) [2 marks] Assume that some liquid SO_2 is contained in a glass cylinder which breaks at a pressure of 700.0 kPa. The amount of SO_2 inside the cylinder is just enough so that there will always some liquid SO_2 left at the working temperatures above the freezing point. At which temperature will this glass cylinder be broken by the inside gas pressure? **State clearly the approximations you have made.**

Part D: [6 marks] The decomposition of CH_3Br is a first-order reaction with an activation energy: E_a = 229.3 kJ/mol. The rate constant at 650 K is found to be 2.14×10^{-4} s^{-1}.

(a) [2 marks] Calculate the pre-exponential factor *A* for this reaction at 650 K.

(b) [2 marks] At a different temperature, say T_2, if the decomposition of 50% CH_3Br takes 10 minutes to complete, evaluate the rate constant at T_2.

(c) [2 marks] Calculate the temperature T_2 in question (b) above.

Part E: **[4 marks]** The following 2nd-order reaction: 2 A(g) → B(g) was carried out at $T = 27$ °C in a reaction vessel of constant volume. At the beginning of the reaction, only A(g) at $P = 1$ atm was present. After 100 minutes of reaction, the total P in the vessel reaches 0.75 atm. Assume that both A(g) and B(g) are ideal gases. Determine the rate constant k and the half-life $t_{1/2}$ of the reaction at 27 °C.

Part F: **[2 marks]** The decomposition of H_2O_2 by the enzyme catalase follows Mechaelis-Menten kinetics. For a solution containing 2 mg of catalase per litre, the following rates of decomposition, v, were measured as a function of the H_2O_2 concentration:

$[H_2O_2]$ (mol L^{-1})	0.002	0.003	0.02	0.03	0.2	0.3	2.0	3.0
v (10^{-3} mol L^{-1} s^{-1})	0.074	0.11	0.45	0.55	0.89	0.92	0.99	0.99

Estimate the Michaelis constant K_M and circle the **two** correct answers from the following.

(a) $K_M \approx 0.25$ mol L^{-1} s^{-1}

(b) $K_M \approx 0.025$ mol L^{-1}

(c) $K_M \approx 0.25$ mol L^{-1}

(d) $K_M \approx 0.025$ L mol^{-1} s^{-1}

(e) $K_M \approx 3.0$ L mol^{-1} s^{-1}

(f) At large H_2O_2 excess, the Michaelis-Menten kinetics is effectively 1st order in H_2O_2.

(g) At large H_2O_2 excess, the Michaelis-Menten kinetics is effectively 0th order in H_2O_2.

(h) The half-life of H_2O_2 is independent of its concentration.

Part G: [12 marks] The decomposition of ozone $2\,O_3(g) \rightarrow 3\,O_2(g)$ has the following mechanism:

1) $O_3 \rightarrow O_2 + O$	rate constant: k_1	$v_1 =$
2) $O + O_2 \rightarrow O_3$	rate constant: k_2	$v_2 =$
3) $O + O_3 \rightarrow 2\,O_2$	rate constant: k_3	$v_3 =$

(a) [3 marks] In the right-most column above, fill in the rate laws for the three elementary reaction steps.

(b) [2 marks] Write down the reaction **rate** in terms of the formation of O_2 using v_1, v_2, and v_3:

(c) [2 marks] Write down the reaction **rate** in terms of the depletion of O_3 using v_1, v_2, and v_3:

(d) [2 marks] Write down the **steady state approximation** for O using v_1, v_2, and v_3:

$$\frac{d[\mathrm{O}]}{dt} =$$

(e) [3 marks] Use the **steady state approximation** to show that the **rate law** for O_3 decomposition follows:

$$v = -\frac{1}{2}\frac{d[\mathrm{O_3}]}{dt} = \frac{k_1 k_3 [\mathrm{O_3}]^2}{k_2[\mathrm{O_2}] + k_3[\mathrm{O_3}]}$$

Part H: **[11 marks]** At 44 °C, a solution of $AlCl_3$ is separated by a membrane. Outside the cell, a double-charged protein ion (whose couter ion is either Al^{3+} or Cl^{-}) is also present. The membrane is permeable to everything in the system except for the protein ion. The equilibrium concentrations of Cl^{-} inside and outside the cell are 0.45 M and 0.15 M, respectively. (**Note**: 0 °C = 273.15 K)

(a) [4 marks] Calculate the equilibrium concentrations of Al^{3+} inside and outside the cell.

(b) [1 mark] Is the protein ion positively or negatively charged? (circle one 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.

(e) [2 marks] Calculate the osmotic pressure difference (in unit **atm**) across the cell membrane after the equilibrium is reached.

Part I: **[10 marks]** We know the following standard reduction potentials, at 25 °C (**Note**: 0 °C = 273.15 K):

$Au^{3+}(aq) + 2\,e^- \rightarrow Au^+(aq)$ $\varepsilon_1° = 1.36$ V
$Au^+(aq) + e^- \rightarrow Au(s)$ $\varepsilon_2° = 1.83$ V

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

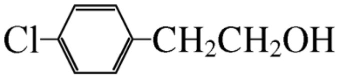
Anode	
Cathode	
Total Cell	

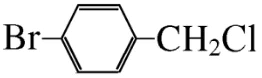
(b) [3 marks] Calculate emf $\varepsilon°$ and $\Delta G°$ for the total cell reaction.

(c) [2 marks] If $[Au^{3+}] = 1.0$ M, at what concentration of $Au^+(aq)$ would the cell become nonspontaneous?

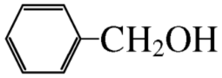
(d) [2 marks] Calculate emf $\varepsilon_3°$ for the half-cell reaction: $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$

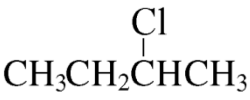
Part J: [6 marks] Assign the correct molecular formula (or structure) to each of the following ^{1}H NMR spectrum. Fill in the box using the appropriate number corresponding to a particular molecule, *e.g.*, $\boxed{8}$. There is only one correct formula (or structure) for each NMR spectrum. Note that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

1)


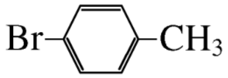
2)


3) $CH_3CH_2CH_3$

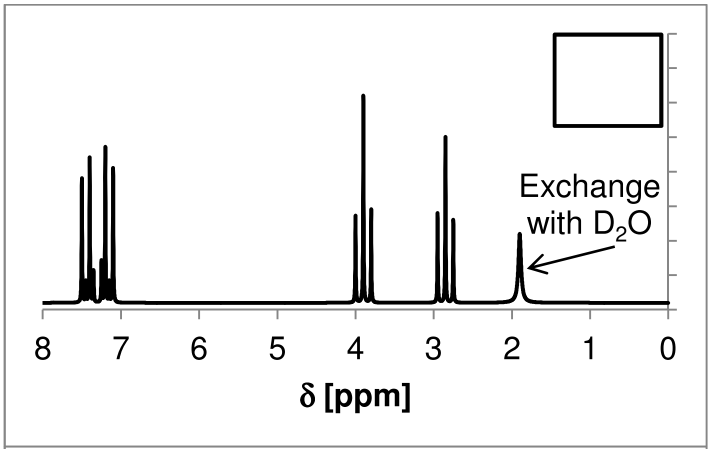
4)


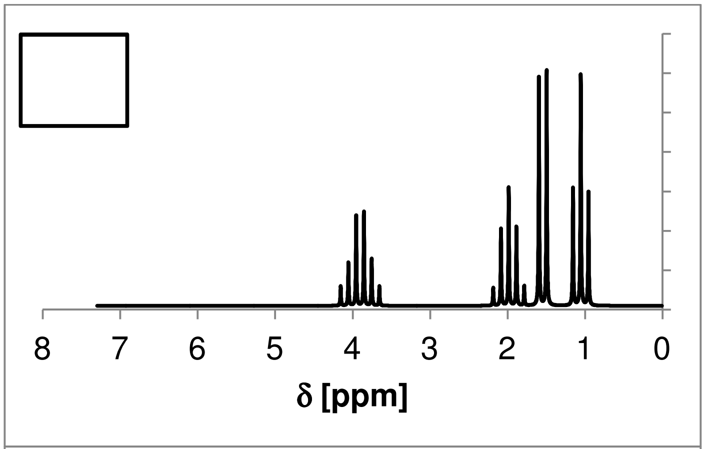
5)

$CH_3CH_2\overset{Cl}{C}HCH_3$

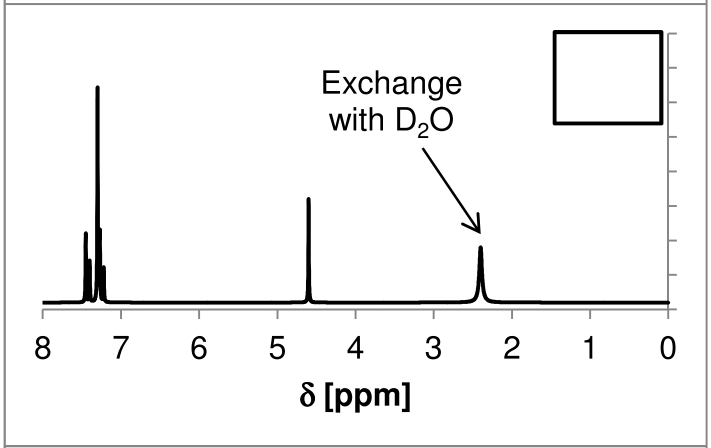
6) $Cl-CH_2CH(CH_3)_2$

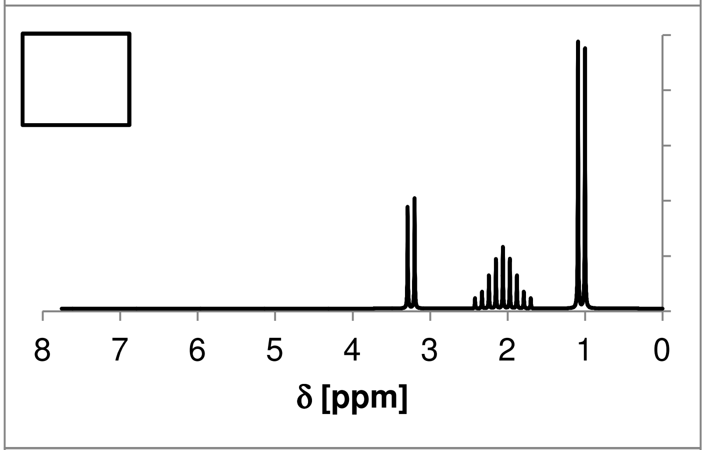
7)


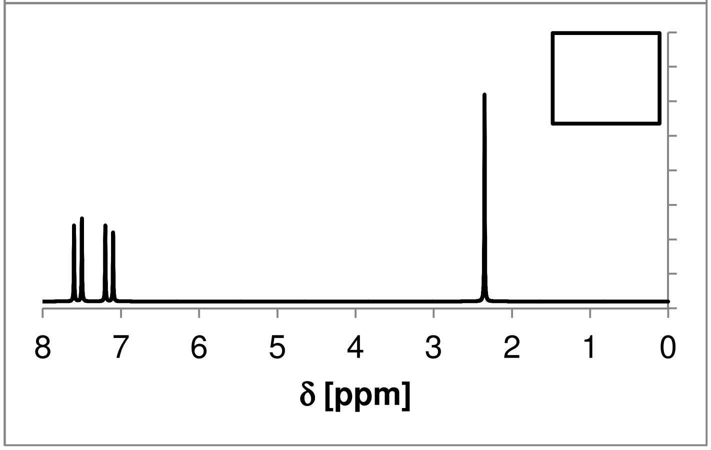
8) $(CH_3)_2CH-Cl$

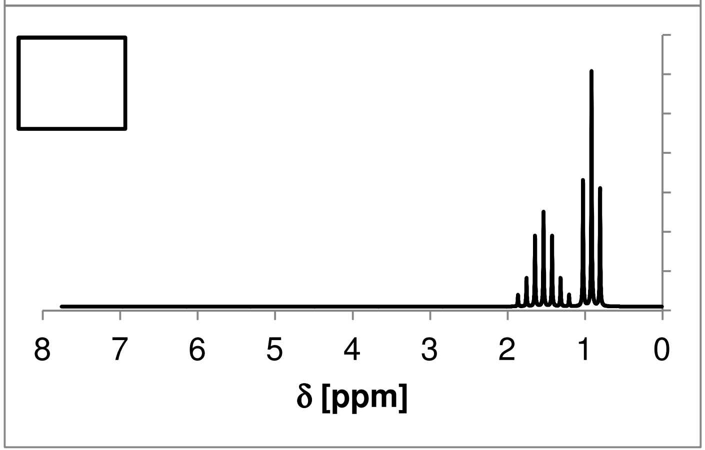




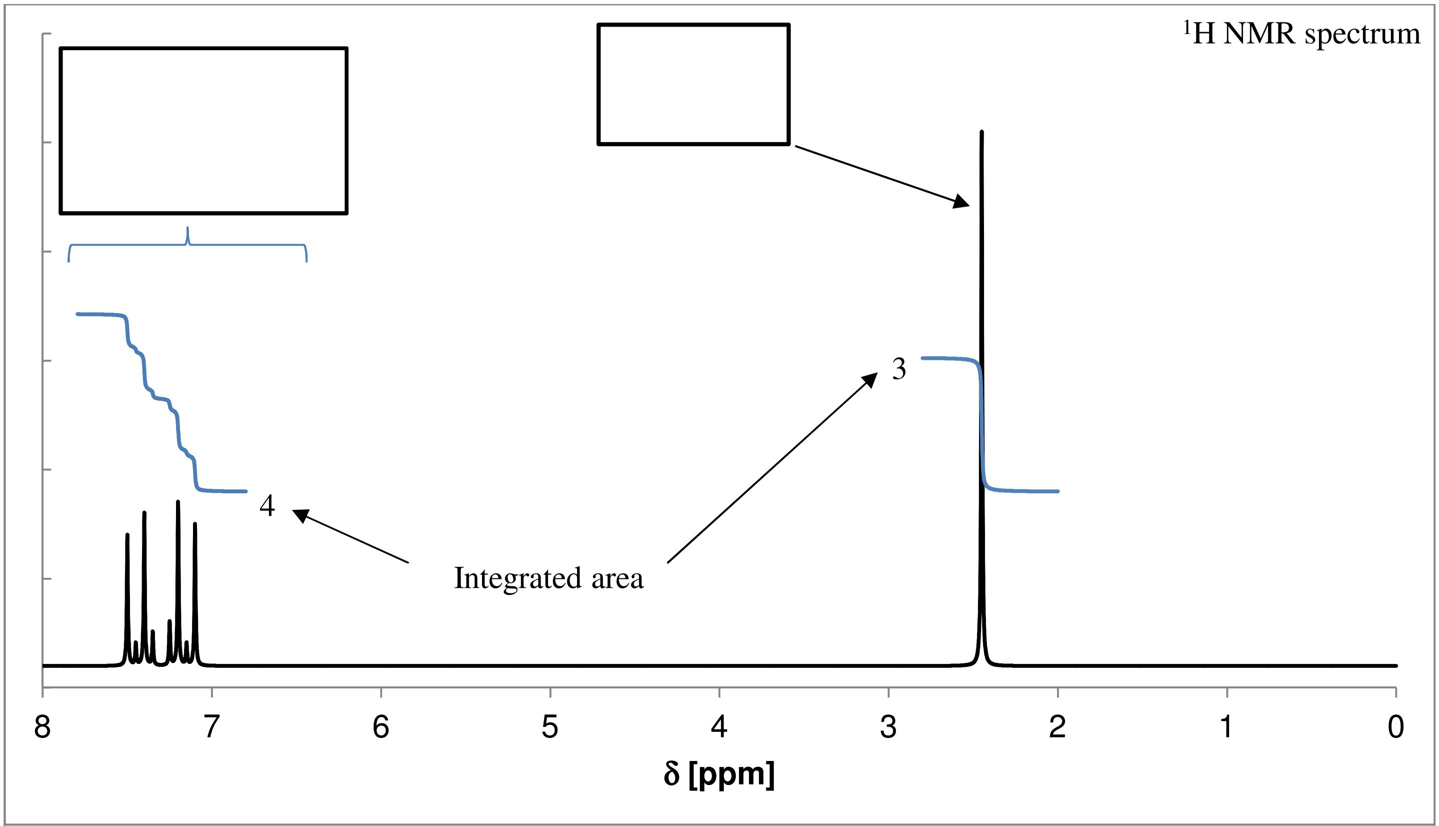


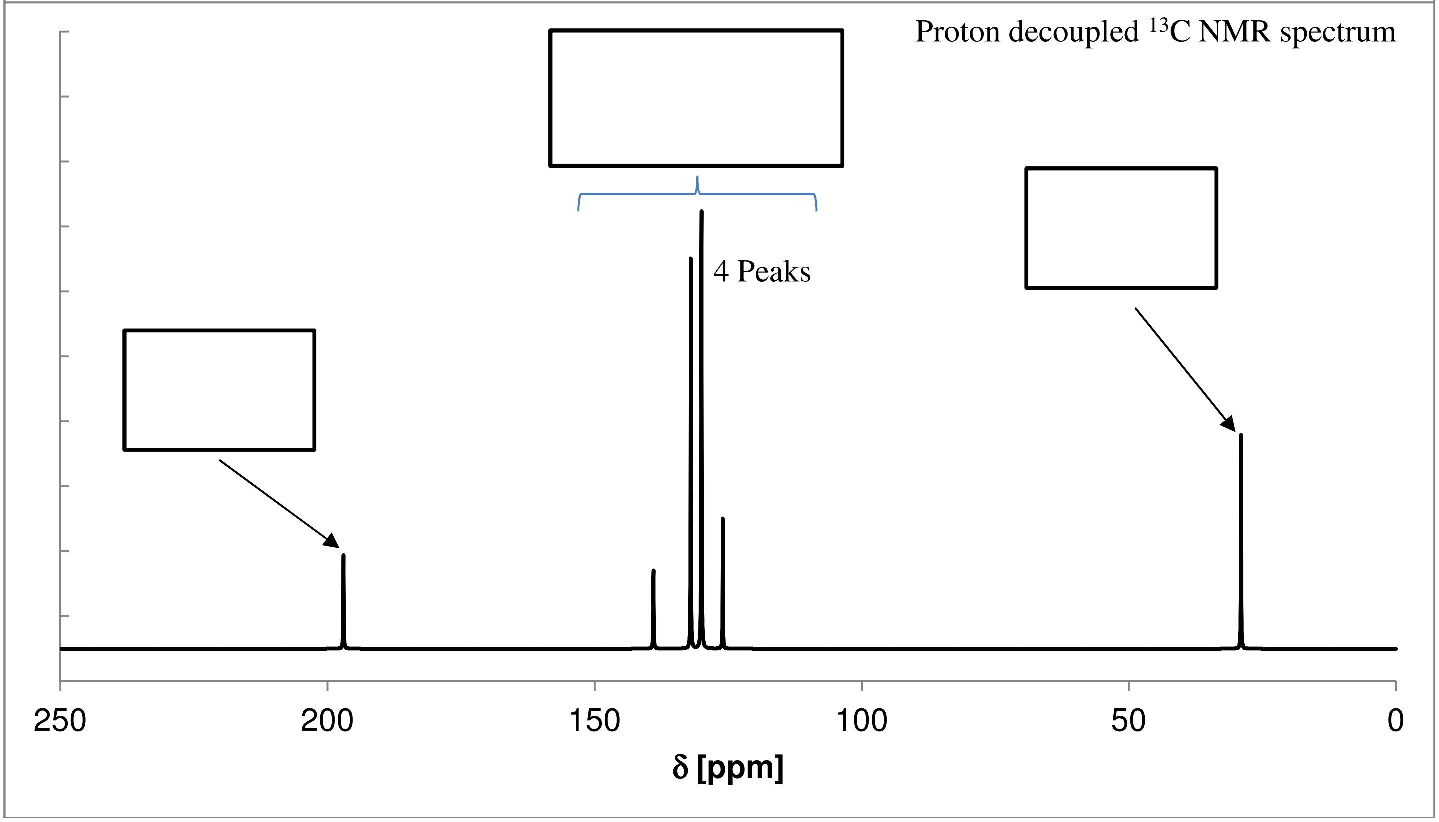


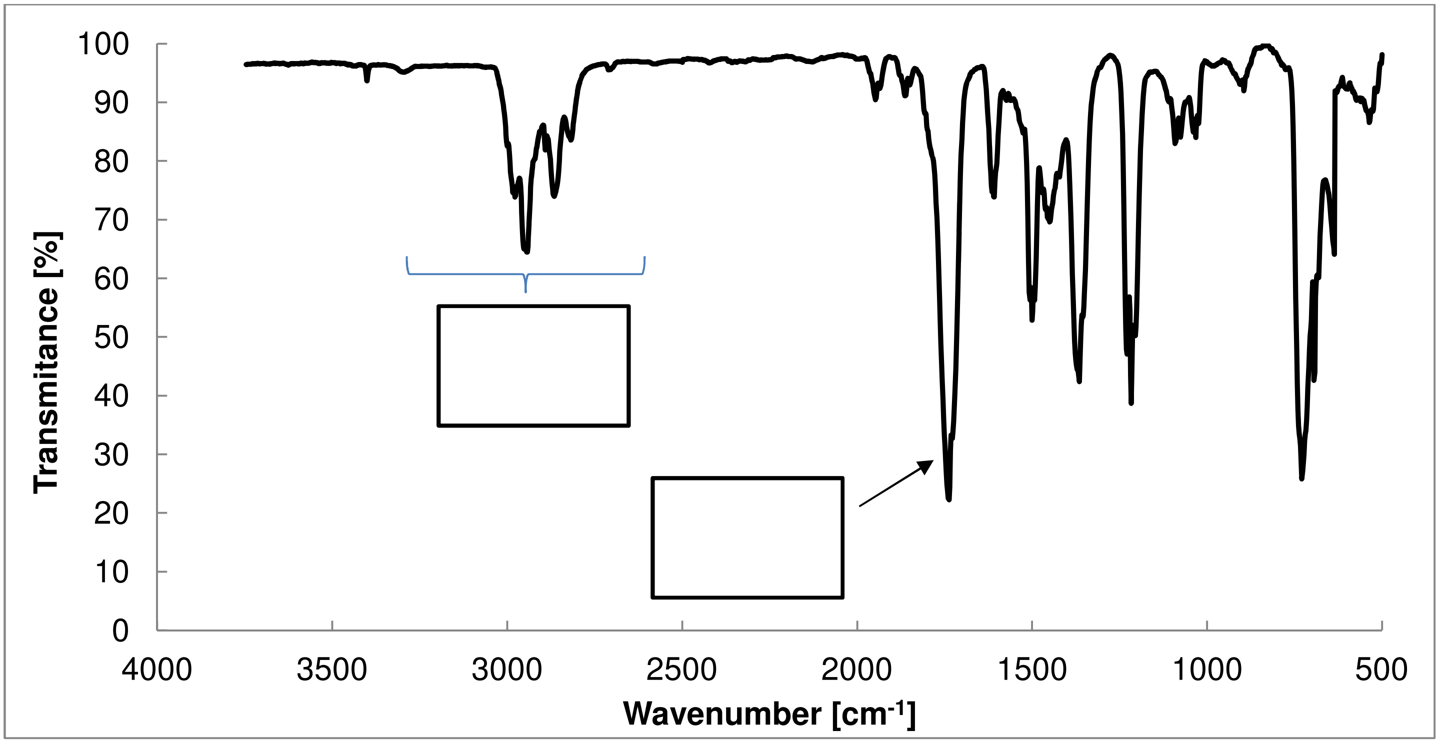


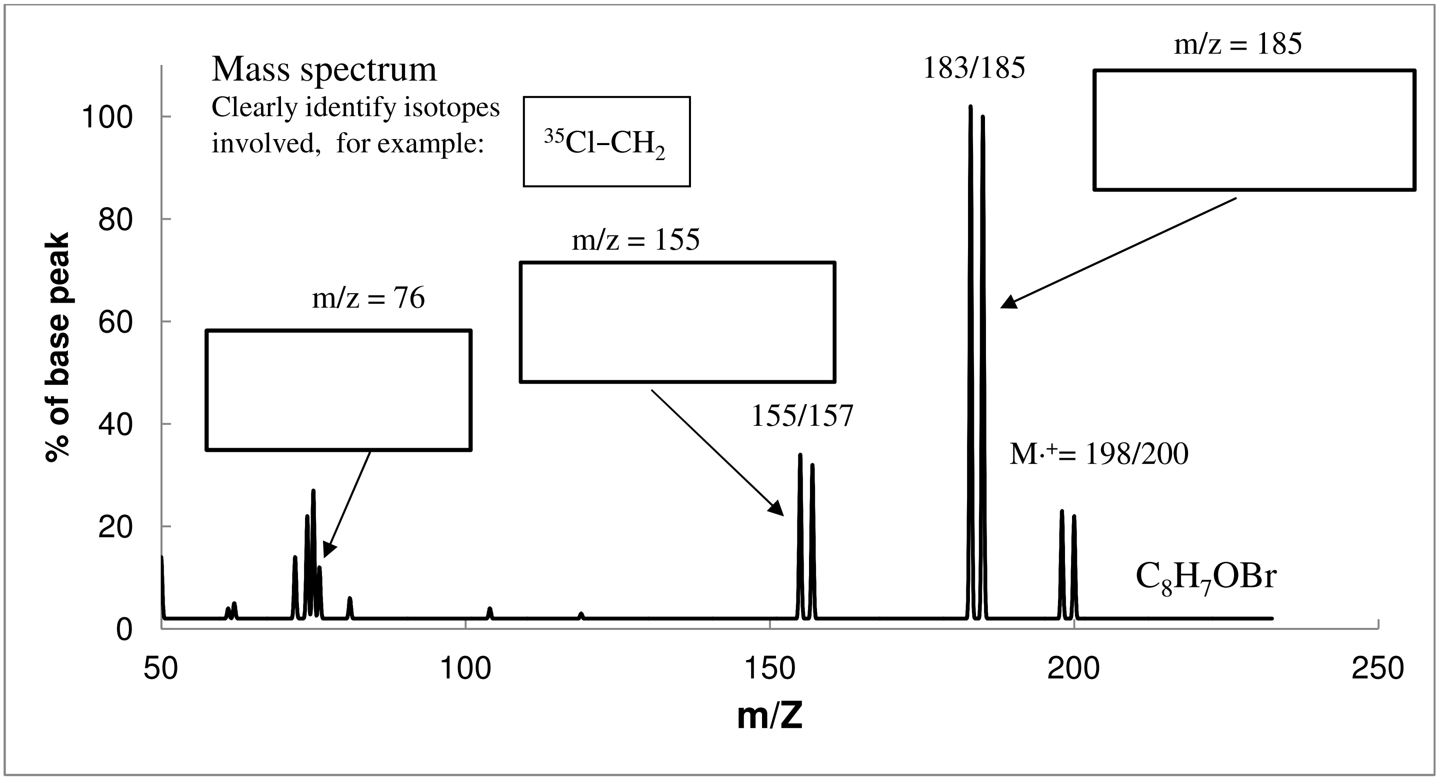


Part K: [11 marks] The following spectra were collected for a compound of formula C_8H_7OBr. Fill the boxes in each spectrum to show which chemical moiety (*e.g.*, $–CH_3$, $–CH_2–$, *etc.*) gives rise to the peaks indicated by bracket or arrow. Identify the compound by drawing its structure in the big empty box on the next page.









UV Spectrum:
λ_{max} 258 nm (log ε = 4.2)
Solvent ethanol

Draw the structure of the molecule in the box:

Equations and Constants

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

$R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}} = 0.08206\ \mathrm{L\ atm\ K^{-1}\ mol^{-1}}$

$k = 1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}}$

$N_\mathrm{A} = 6.0221 \times 10^{23}\ \mathrm{mol^{-1}}$

$F = 96485\ \mathrm{C\ mol^{-1}}$

$0\ °\mathrm{C} = 273.15\ \mathrm{K}$

$1\ \mathrm{atm} = 101325\ \mathrm{Pa}$

$1\ \mathrm{L} = 0.001\ \mathrm{m^3}$

$1\ \mathrm{L\ atm} = 101.325\ \mathrm{J}$

$$PV = nRT$$

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

$$\Delta U = U_2 - U_1 = q + w$$

$$dw = -P_\mathrm{ex}dV$$

$$w = -P_\mathrm{ex}(V_2 - V_1)$$

$$w = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

$$dq = C \cdot dT$$

$$C_V = nC_{V,m} = \frac{dq_V}{dT}$$

$$\Delta U = q_V = \int_{T_1}^{T_2} nC_{V,m}dT = \int_{T_1}^{T_2} C_V dT$$

$$H = U + PV$$

$$C_P = nC_{P,m} = \frac{dq_P}{dT}$$

$$\Delta H = q_P = \int_{T_1}^{T_2} nC_{P,m}dT = \int_{T_1}^{T_2} C_P dT$$

$$\Delta H^0_\mathrm{rxn} = \sum_i \nu_i \Delta H^0_{m,i}(\text{products}) - \sum_j \nu_j \Delta H^0_{m,j}(\text{reatants})$$

$$C_{V,m} = \frac{3}{2}R, \quad C_{P,m} = \frac{5}{2}R$$

$$dS = dq_\mathrm{rev}/T$$

$$\Delta S = S_2 - S_1 = \int_{\text{state 1}}^{\text{state 2}} \frac{dq_\mathrm{rev}}{T}$$

$$(\Delta S)_{T,P} = \Delta H/T$$

$$(\Delta S)_T = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right)$$

$$(\Delta S)_V = nC_{V,m}\ln\left(\frac{T_2}{T_1}\right)$$

$$(\Delta S)_P = nC_{P,m}\ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = nC_{V,m}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nC_{P,m}\ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)$$

$$\Delta S_\mathrm{univ} = \Delta S_\mathrm{sys} + \Delta S_\mathrm{surr}$$

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H^0_{\mathrm{vap},m}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0_\mathrm{rxn}}{(1\ \mathrm{mol})\cdot R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\mathrm{F} = \mathrm{C} - \mathrm{P} + 2$$

$$G = H - TS$$

$$\Delta G_{T,P} = -T\cdot\Delta S_\mathrm{univ}$$

$$\Delta G_\mathrm{rxn} = \Delta G^0_\mathrm{rxn} + (1\ \mathrm{mol})\cdot RT\ln Q$$

$$\Delta G^0_\mathrm{rxn} = -(1\ \mathrm{mol})\cdot RT\ln K$$

$$\Delta G_\mathrm{rxn} = -nF\varepsilon, \quad \Delta G^0_\mathrm{rxn} = -nF\varepsilon^0$$

$$\varepsilon = \varepsilon^0 - \frac{(1\ \mathrm{mol})\cdot RT}{nF}\ln Q$$

$$\Delta T_\mathrm{b} = T_\mathrm{b,mix} - T_\mathrm{b,pure} \approx K_\mathrm{b} b_B$$

$$\Delta T_\mathrm{f} = T_\mathrm{f,mix} - T_\mathrm{f,pure} \approx -K_\mathrm{f} b_B$$

$$\Pi = c_B RT$$

$$\Delta\Pi = \Delta c \cdot RT$$

$$\varepsilon \approx \frac{-RT}{z_i F}\ln\left(\frac{[i]_\mathrm{R}}{[i]_\mathrm{L}}\right)$$

$$T = \frac{I}{I_0}$$

$$A = -\log_{10} T = lc\varepsilon$$

$$v = k[\mathrm{A}]^a[\mathrm{B}]^b[\mathrm{C}]^c\cdots$$

$$a\mathrm{A} \rightarrow \mathrm{B}: \quad v = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n$$

$$a\mathrm{A} \rightarrow \mathrm{B}: \quad [\mathrm{A}] = [\mathrm{A}]_0 - akt, \quad t_{1/2} = \frac{[\mathrm{A}]_0}{2ak}$$

$$a\mathrm{A} \rightarrow \mathrm{B}: \quad \ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -akt, \quad t_{1/2} = \frac{\ln 2}{ak}$$

$$a\mathrm{A} \rightarrow \mathrm{B}: \quad \frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0} = akt, \quad t_{1/2} = \frac{1}{ak[\mathrm{A}]_0}$$

$$t = \frac{t_{1/2}}{\ln 0.5}\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right), \quad \frac{[\mathrm{A}]}{[\mathrm{A}]_0} = 0.5^{\frac{\text{time}}{\text{half-life}}}$$

$$K = \frac{k_1}{k_1'}\times\frac{k_2}{k_2'}\times\frac{k_3}{k_3'}\times\cdots$$

$$k = Ae^{\frac{-E_a}{RT}} = A\exp\left(\frac{-E_a}{RT}\right)$$

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

$$v = \frac{[\mathrm{S}]\cdot v_\mathrm{max}}{[\mathrm{S}] + K_\mathrm{M}}, \quad v_\mathrm{max} = k_b[\mathrm{E}]_\mathrm{tot}$$

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**
$RC\mathbf{H}_3$	0.8 − 1.0
$RC\mathbf{H}_2R$	1.2 − 1.4
$R_3C\mathbf{H}$	1.4 − 1.7
$R_2C{=}C(R){-}C\mathbf{H}_3$	1.6 − 1.9
$ArC\mathbf{H}_3$ (Ar is benzene ring)	2.2 − 2.5
$RC\mathbf{H}_2Cl$	3.6 − 3.8
$RC\mathbf{H}_2Br$	3.4 − 3.6
$RC\mathbf{H}_2I$	3.1 − 3.3
$ROC\mathbf{H}_2R$	3.3 − 3.9
$RC\mathbf{H}_2OH$	3.3 − 4.0
$RC(=O)C\mathbf{H}_3$	2.1 − 2.6
$RC(=O)\mathbf{H}$	9.5 − 9.6
$R_2C{=}C\mathbf{H}_2$	4.6 − 5.0
$R_2C{=}C(R)\mathbf{H}$	5.2 − 5.7
$Ar\mathbf{H}$	6.0 − 9.5
$RC{\equiv}C\mathbf{H}$	2.5 − 3.1
$RO\mathbf{H}$	0.5 − 6.0
$RC(=O)O\mathbf{H}$	10 – 13
$ArO\mathbf{H}$	4.5 − 7.7
$R{-}N\mathbf{H}_2$	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 **17** 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 **15** pages in this booklet. Only the work written on the first **15** 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
13 April 2019, 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	10	
Part C	8	
Part D	6	
Part E	4	
Part F	2	
Part G	12	
Part H	11	
Part I	10	
Part J	6	
Part K	11	
Total	100	

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

1. [1 mark] If the order of a chemical reaction (in the rate law) is −1, the units of the rate constant is

[✓ 1) mol^2 L^{-2} s^{-1}] 2) mol L^{-1} s^{-1} 3) L mol^{-1} s^{-1} 4) L^2 mol^{-2} s^{-1} 5) s^{-1}

2. [1 mark] A sample of an ideal gas, contained within a closed vessel, undergoes some process starting from 1 atm and 2 L and arriving at 4 atm and 0.5 L. Which one of the following statements is always true?

1) During the entire process, T is a constant.

2) During the entire process, U is a constant.

3) During the entire process, H is a constant.

[✓ 4) $\Delta H = H_{\text{final}} - H_{\text{initial}} = 0$.]

5) $q > 0$.

3. [1 mark] A peak in an NMR spectrum of a molecule directly represents

1) a nuclear spin state of the molecule.

2) an electron spin transition of the molecule.

3) a vibrational transition of the molecule.

4) a rotational transition of the molecule.

[✓ 5) none of the above.]

4. [1 mark] Elementary termolecular reactions are normally very slow because

1) elementary termolecular reactions take many steps to finish.

2) a termolecular reaction is made of a unimolecular reaction and a dimolecular reaction.

3) the more molecules collide at the same time, the faster the elementary reaction will proceed.

[✓ 4) the probability for three molecules to collide at the same time is low.]

5) none of the above.

5. [1 mark] A dye solution of concentration 0.1 mol/L was measured to have a transmittance of 0.1 at 550 nm. The path length of the light passing through the solution was 1 cm. What is the molar extinction coefficient (molar absorptivity) of the dye molecule?

1) 1 L^{-1} mol^{-1} cm^{-1} 2) 10 m^3 mol^{-1} cm^{-1} 3) 1 L mol^{-1} m^{-1} [✓ 4) 10 L mol^{-1} cm^{-1}] 5) 10 L^{-1} mol^{-1} cm^{-1}

6. [1 mark] For a given chemical reaction happening at a fixed temperature,

[✓ 1) a catalyst can only change the rate constants.]

2) a catalyst can only change the forward reaction's rate constant.

3) a catalyst can only change the equilibrium constant.

4) a catalyst can change both the rate constant and the equilibrium constant.

5) a catalyst can change neither the rate constant nor the equilibrium constant.

7. [1 mark] The following statement for chemical equilibrium applies to the equation: $\Delta G = \Delta G^\circ + RT \ln Q$

1) At equilibrium, $Q = 0$ and $\Delta G = 0$.

2) At equilibrium, $\Delta G^\circ = 0$ and $Q = K$.

3) Because $\Delta G^\circ = -RT \ln K$, ΔG° is a measure of the Gibbs energy difference between products and reactants at equilibrium.

4) At equilibrium, $\Delta G^\circ = \Delta G$ and $Q = 1$.

[✓ 5) None of the above.]

8. [1 mark] Using IR spectroscopy, we **cannot** observe the vibrational modes in

1) CO 2) H_2O [✓ 3) Xe] 4) CO_2 5) CH_4

9. [1 mark] To calculate the expansion work for a process,

1) the formula $w = -P_{ex}(V_2 - V_1)$ always works under all conditions.

2) the formula $dw = -P_{ex}\,dV$ can only be used for irreversible processes.

[✓ 3) the formula $dw = -P_{ex}\,dV$ always works under all conditions.]

4) the formula $w = -nRT \ln(V_2/V_1)$ always works for any isothermal reversible process.

5) None of the above is applicable.

10. [1 mark] Upon reaching equilibrium during an osmosis process across a semipermeable membrane of a biological cell between fresh water (outside the cell) at **2 atm** pressure and a salt solution (inside the cell), what is the pressure P exerted on the side of the salt solution?

1) $P = 1$ atm

2) $P = 2$ atm

3) $P = \Pi$ (the osmotic pressure)

[✓ 4) $P = \Pi + 2$ atm]

5) $P = \Pi + 1$ atm

11. [1 mark] If a **proposed** chemical reaction is exothermic and results in a decrease in the entropy of the system, this chemical reaction:

1) will proceed forward spontaneously.
2) will proceed backward spontaneously.
3) will be in equilibrium.
4) will not react at all.
[✓ 5) The information given is insufficient to determine the spontaneity of the reaction.]

12. [1 mark] Which one of the following statements about electromagnetic radiation is correct?

1) Infrared light is in red color.
2) Ultraviolet light has extremely violet color.
3) X-ray is in black and white.
4) Visible light is always white unless it is in the rainbows.
[✓ 5) None of the above.]

13. [1 mark] In a rundown AA alkaline battery just taken out of an old toy,

1) no more energy can be supplied because the battery is no longer in equilibrium condition.
2) no more energy can be supplied because all reactants are used up.
3) no more energy can be supplied because there are no electrons left in the battery.
[✓ 4) no more energy can be supplied because the reactants and products of the electrochemical reaction is approaching equilibrium.]
5) the ΔG of the system is negative.

14. [1 mark] At the same temperature and pressure, the equilibrium constant of the first reaction $2\,A(g) + 2\,B(g) \rightleftharpoons D(g)$ is K_1, and the equilibrium constant of the second reaction $\frac{1}{2}D(g) \rightleftharpoons A(g) + B(g)$ is K_2, which one of the following statements is correct?

1) $K_2 = -K_1$ 2) $K_2 = K_1$ 3) $K_2 = (K_1)^{0.5}$ [✓ 4) $K_2 = (K_1)^{-0.5}$] 5) None of the above

15. [1 mark] For a unimolecular dissociation reaction: $A_2 \rightarrow 2\,A$, the change of the amount of the product per unit time, C_A, and the average rate of this reaction, v_{mean}, are related according to

1) $C_A = v_{\text{mean}}$ 2) $2\,C_A = v_{\text{mean}}$ [✓ 3) $C_A = 2\,v_{\text{mean}}$] 4) $2\,C_A = -v_{\text{mean}}$ 5) $C_A = -2\,v_{\text{mean}}$

16. [1 mark] The decomposition of O_3 in the upper atmosphere, $2O_3(g) \rightarrow 3O_2(g)$, **involves** the following two elementary reactions in the mechanism:

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$$

$$O_3 + ClO\cdot \rightarrow Cl\cdot + 2\,O_2$$

Which one of the following statements concerning the above reaction is true?

1) Neither ClO· nor Cl· is an intermediate or a catalyst.

2) ClO· is an intermediate; Cl· is a catalyst.

3) ClO· is a catalyst; Cl· is an intermediate.

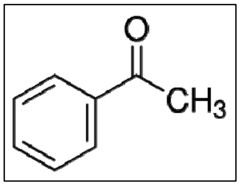
4) Both ClO· and Cl· are catalysts.

[✓ 5) We cannot tell from the given information whether a catalyst is present.]

17. [1 mark] Two moles of a monatomic ideal gas is confined within a two-dimensional plane at constant T. What is the internal energy of this system according to the Equipartition Principle?

1) RT 2) $(1/2)\cdot RT$ [✓ 3) $2\,RT$] 4) $(3/2)\cdot RT$ 5) $3\,RT$

18. [1 mark] Which one of the following is **not** true regarding the spectra of acetophenone $C_6H_5{-}CO{-}CH_3$:



1) in the ^{1}H NMR, the CH_3 group will appear as a singlet.

2) the ^{13}C NMR will have a singlet at approximately 200 ppm.

[✓ 3) the IR spectrum will display a significant absorption at about 2400 cm^{-1}.]

4) in the ^{1}H NMR, the CH_3 group will absorb at approximately $\delta = 2.2$ ppm.

5) in the mass spectrum, a significant peak will occur at m/z = 43.

19. [1 mark] The maximum number of coexisting phases for a mixture of toluene, benzene, and acetone is

1) 1 2) 2 3) 3 4) 4 [✓ 5) 5]

20. [1 mark] After adding some table salt to a cup of pure water, how do the boiling point and freezing point of the salt solution change with respect to those of pure water?

1) Both the boiling point and freezing point of the salt solution stay the same.

2) Both the boiling point and freezing point of the salt solution decrease.

3) Both the boiling point and freezing point of the salt solution increase.

[✓ 4) The boiling point of the salt solution increases whereas the freezing point of the salt solution decreases.]

5) The boiling point of the salt solution decreases whereas the freezing point of the salt solution increases

Part B: **[10 marks]** Three moles of an ideal gas undergoes an isothermal process at $T = 25$ °C, from an initial pressure of 1 atm to a final pressure of 3 atm. Throughout the entire process, the external pressure on the gas is maintained equal to the final pressure of the gas, and the temperature of the surroundings is also kept the same as the temperature of the system. (**Note**: 0 °C = 273.15 K)

(a) [5 marks] Calculate w, q, ΔU, and ΔH for this process.

$$\text{(a)}\ \left\{\begin{array}{l} p_iV_i = nRT_i \ \Rightarrow\ V_i = \dfrac{nRT_i}{p_i} = \dfrac{3\times 0.08206\times 298.15}{1} = 73.40\ \text{L} \\ p_fV_f = nRT_f \ \Rightarrow\ V_f = \dfrac{nRT_f}{p_f} = \dfrac{3\times 0.08206\times 298.15}{3} = 24.47\ \text{L} \\ \Delta V = V_f - V_i = 24.47 - 73.40 = -48.93\ \text{L} \\ w = -p_{ex}\cdot\Delta V = -3\times(-48.93)\times 101.325 = 14873.5\ \text{J}\ \ (14.9\ \text{kJ}) \\ dT = 0\ \text{for ideal gas}\ \Rightarrow\ \Delta U = 0,\ \ \Delta H = 0 \\ \Delta U = q + w = 0\ \Rightarrow\ q = -w = -14873.5\ \text{J}\ \ (-14.9\ \text{kJ}) \end{array}\right.$$

$$\text{OR}:\ \left\{\begin{array}{l} \left.\begin{array}{l} w = -p_{ex}\cdot\Delta V = -p_f\cdot\left(V_f - V_i\right) \\ p_iV_i = nRT = p_fV_f\ \Rightarrow\ V_i = \dfrac{p_fV_f}{p_i} \end{array}\right\}\ \Rightarrow\ w = \left(\dfrac{p_f}{p_i} - 1\right)\cdot nRT \\ w = \left(\dfrac{3}{1} - 1\right)\times 3\times 8.314\times 298.15 = 14872.9\ \text{J}\ \ (14.9\ \text{kJ}) \end{array}\right.$$

(b) [4 marks] Calculate ΔS_{system} and ΔG for this process.

$$\text{(b)}\ \left\{\begin{array}{l} \Delta S = nR\ln\dfrac{V_f}{V_i} = nR\ln\dfrac{p_i}{p_f} = 3\times 8.314\times\ln\dfrac{1}{3} = -27.4\ \text{J/K} \\ \Delta G = \Delta H - T\cdot\Delta S = -T\cdot\Delta S = -298.15\times(-27.4) = 8169.3\ \text{J}\ \ (8.17\,\text{kJ}) \end{array}\right.$$

(c) [1 mark] Is the process spontaneous? (circle the **only one** correct answer below)

[✓ 1) Yes] 2) No 3) Can be either spontaneous or nonsponstaneous

$$\text{(c)}\ \left\{\begin{array}{l} \Delta S_{surr} = -\dfrac{q}{T} = \dfrac{14872.9}{298.15} = 49.9\ \text{J/K} \\ \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -27.4 + 49.9 = 22.5\ \text{J/K}\ >\ 0 \end{array}\right.$$

Part C: [8 marks] The following vapor pressures were measured for SO_2 gas in equilibrium with liquid SO_2:

T (°C)	−46.9	6.3
P (kPa)	1.333	20.270

(a) [6 marks] Calculate ΔG, ΔH, and ΔS for the vaporization of SO_2 at 6.3 °C and 20.270 kPa. (**Note**: 0 °C = 273.15 K)

$$\text{(a)}\ \begin{cases} \Delta G = 0 \text{ for vaporization in equilibrium at } 6.3\,^{\circ}\text{C}. \\ \ln\left(\dfrac{p_2}{p_1}\right) = -\dfrac{\Delta H}{R}\left(\dfrac{1}{T_2}-\dfrac{1}{T_1}\right) \Rightarrow \Delta H = \dfrac{-R\ln\left(\dfrac{p_2}{p_1}\right)}{\left(\dfrac{1}{T_2}-\dfrac{1}{T_1}\right)} = 26892.6 \text{ J } (26.9 \text{ kJ}) \\ \Delta G = \Delta H - T\cdot\Delta S = 0 \Rightarrow \Delta S = \dfrac{\Delta H}{T} = \dfrac{26892.6}{279.45} = 96.2 \text{ J/K} \end{cases}$$

(b) [2 marks] Assume that some liquid SO_2 is contained in a glass cylinder which breaks at a pressure of 700.0 kPa. The amount of SO_2 inside the cylinder is just enough so that there will always some liquid SO_2 left at the working temperatures above the freezing point. At which temperature will this glass cylinder be broken by the inside gas pressure? **State clearly the approximations you have made.**

$$\text{(b)}\ \begin{cases} \text{Assume } \Delta H \ \&\ \Delta S \text{ independent of } T \\ \ln\left(\dfrac{p_2}{p_1}\right) = -\dfrac{\Delta H}{R}\left(\dfrac{1}{T_2}-\dfrac{1}{T_1}\right) \Rightarrow \dfrac{1}{T_2} = \dfrac{1}{T_1} - \dfrac{R}{\Delta H}\ln\left(\dfrac{p_2}{p_1}\right) \\ T_2 = 402.7 \text{ K } (403 \text{ K}) \end{cases}$$

Part D: [6 marks] The decomposition of CH_3Br is a first-order reaction with an activation energy: E_a = 229.3 kJ/mol. The rate constant at 650 K is found to be $2.14 \times 10^{-4}\ s^{-1}$.

(a) [2 marks] Calculate the pre-exponential factor A for this reaction at 650 K.

$$\text{(a)} \begin{cases} k = A \cdot e^{\frac{-E_a}{RT}} \Rightarrow A = k \cdot e^{\frac{E_a}{RT}} \\ A = 2.14 \times 10^{-4} \times \exp\left(\dfrac{229.3 \times 10^3}{8.314 \times 650}\right) = 5.73 \times 10^{14}\ \ s^{-1} \end{cases}$$

(b) [2 marks] At a different temperature, say T_2, if the decomposition of 50% CH_3Br takes 10 minutes to complete, evaluate the rate constant at T_2.

$$\text{(b)} \begin{cases} t_{1/2} = 10\ \ \text{min} = 600\ \ s \\ t_{1/2} = \dfrac{\ln 2}{k_2} \Rightarrow k_2 = \dfrac{\ln 2}{t_{1/2}} = \dfrac{\ln 2}{600} = \begin{cases} 0.001155\ \ s^{-1} \\ 11.55 \times 10^{-4}\ \ s^{-1} \\ 1.155 \times 10^{-3}\ \ s^{-1} \\ 0.06931\ \ \text{min}^{-1} \end{cases} \end{cases}$$

(c) [2 marks] Calculate the temperature T_2 in question (b) above.

$$\text{(c)} \begin{cases} \ln\left(\dfrac{k_1}{k_2}\right) = -\dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right) \Rightarrow \dfrac{1}{T_2} = \dfrac{1}{T_1} + \dfrac{R}{E_a}\ln\left(\dfrac{k_1}{k_2}\right) \\ \text{OR}:\ k_2 = Ae^{\frac{-E_a}{RT_2}} \Rightarrow \dfrac{1}{T_2} = \dfrac{R}{E_a}\ln\left(\dfrac{A}{k_2}\right) \\ T_2 = 676.9\ \ K\ \ (677\ \ K) \end{cases}$$

Part E: **[4 marks]** The following 2nd-order reaction: 2 A(*g*) → B(*g*) was carried out at $T = 27$ °C in a reaction vessel of constant volume. At the beginning of the reaction, only A(*g*) at $P = 1$ atm was present. After 100 minutes of reaction, the total P in the vessel reaches 0.75 atm. Assume that both A(*g*) and B(*g*) are ideal gases. Determine the rate constant k and the half-life $t_{1/2}$ of the reaction at 27 °C.

	2A	→	B
I	1 atm		0
C	$2x$		x
E	$1-2x$		x

$$\begin{cases} P_{\text{tot}} = (1-2x)+x = 1-x = 0.75 \;\Rightarrow\; x = 0.25\ \text{atm} \\ P_{\text{A}} = 1-2x = 0.50\ \text{atm} \\ \text{Because } (P_{\text{A}})_{t=100\,\text{min}} = \dfrac{1}{2}(P_{\text{A}})_{t=0\,\text{min}} \\ \text{Thus, } t_{1/2} = 100\ \text{min} \end{cases}$$

$$\begin{cases} \dfrac{1}{[\text{A}]} - \dfrac{1}{[\text{A}]_0} = 2kt \;\Rightarrow\; k = \dfrac{1}{2t}\left(\dfrac{1}{[\text{A}]} - \dfrac{1}{[\text{A}]_0}\right) = \dfrac{1}{2\times100}\left(\dfrac{1}{0.50} - \dfrac{1}{1.00}\right) = \begin{cases} 5.00\times10^{-3}\ \text{atm}^{-1}\ \text{min}^{-1} \\ 0.005\ \text{atm}^{-1}\ \text{min}^{-1} \end{cases} \\ \text{OR: } t_{1/2} = \dfrac{1}{2k[\text{A}]_0} \;\Rightarrow\; k = \dfrac{1}{2t_{1/2}[\text{A}]_0} = \dfrac{1}{2\times100\times1.00} = 0.005\ \text{atm}^{-1}\ \text{min}^{-1} \end{cases}$$

Part F: **[2 marks]** The decomposition of H_2O_2 by the enzyme catalase follows Mechaelis-Menten kinetics. For a solution containing 2 mg of catalase per litre, the following rates of decomposition, *v*, were measured as a function of the H_2O_2 concentration:

$[H_2O_2]$ (mol L^{-1})	0.002	0.003	0.02	0.03	0.2	0.3	2.0	3.0
v (10^{-3} mol L^{-1} s^{-1})	0.074	0.11	0.45	0.55	0.89	0.92	0.99	0.99

Estimate the Michaelis constant K_M and circle the **two** correct answers from the following.

(a) $K_M \approx 0.25$ mol L^{-1} s^{-1}

[✓ (b) $K_M \approx 0.025$ mol L^{-1}]

(c) $K_M \approx 0.25$ mol L^{-1}

(d) $K_M \approx 0.025$ L mol^{-1} s^{-1}

(e) $K_M \approx 3.0$ L mol^{-1} s^{-1}

(f) At large H_2O_2 excess, the Michaelis-Menten kinetics is effectively 1st order in H_2O_2.

[✓ (g) At large H_2O_2 excess, the Michaelis-Menten kinetics is effectively 0th order in H_2O_2.]

(h) The half-life of H_2O_2 is independent of its concentration.

$$\begin{cases} \text{M}-\text{M Eq: } \text{v} = \dfrac{\text{v}_{\max}[\text{S}]}{[\text{S}]+K_M} \;\Rightarrow\; \text{When v} = \dfrac{\text{v}_{\max}}{2},\ K_M = [\text{S}] \\ \text{When } [\text{S}] >> K_M,\ \text{v} \cong \dfrac{\text{v}_{\max}[\text{S}]}{[\text{S}]} = \text{v}_{\max} \;\Rightarrow\; \text{0th order in [S]} \end{cases}$$

Part G: [12 marks] The decomposition of ozone $2\,O_3(g) \rightarrow 3\,O_2(g)$ has the following mechanism:

1) $O_3 \rightarrow O_2 + O$	rate constant: k_1	$v_1 = k_1[O_3]$
2) $O + O_2 \rightarrow O_3$	rate constant: k_2	$v_2 = k_2[O][O_2]$
3) $O + O_3 \rightarrow 2\,O_2$	rate constant: k_3	$v_3 = k_3[O][O_3]$

(a) [3 marks] In the right-most column above, fill in the rate laws for the three elementary reaction steps.

(b) [2 marks] Write down the reaction **rate** in terms of the formation of O_2 using v_1, v_2, and v_3:

$$\text{(b)}\ \begin{cases} v = \dfrac{1}{3}\dfrac{d[O_2]}{dt} = \dfrac{1}{3}(v_1 - v_2 + 2v_3) \\ v = \dfrac{1}{3}(k_1[O_3] - k_2[O][O_2] + 2k_3[O][O_3]) \end{cases}$$

(c) [2 marks] Write down the reaction **rate** in terms of the depletion of O_3 using v_1, v_2, and v_3:

$$\text{(c)}\ \begin{cases} v = -\dfrac{1}{2}\dfrac{d[O_3]}{dt} = -\dfrac{1}{2}(-v_1 + v_2 - v_3) = \dfrac{1}{2}(v_1 - v_2 + v_3) \\ v = -\dfrac{1}{2}(-k_1[O_3] + k_2[O][O_2] - k_3[O][O_3]) \\ v = \dfrac{1}{2}(k_1[O_3] - k_2[O][O_2] + k_3[O][O_3]) \end{cases}$$

(d) [2 marks] Write down the **steady state approximation** for O using v_1, v_2, and v_3:

$$\text{(d)}\ \begin{cases} \dfrac{d[O]}{dt} = v_1 - v_2 - v_3 = 0 \ \Rightarrow\ v_1 = v_2 + v_3 \\ k_1[O_3] - k_2[O][O_2] - k_3[O][O_3] = 0 \\ k_1[O_3] = k_2[O][O_2] + k_3[O][O_3] \\ [O] = \dfrac{k_1[O_3]}{k_2[O_2] + k_3[O_3]} \end{cases}$$

(e) [3 marks] Use the **steady state approximation** to show that the **rate law** for O_3 decomposition follows:

$$\text{(e)}\ \begin{cases} \dfrac{d[O]}{dt} = 0 \ \Rightarrow\ v_1 = v_2 + v_3 \ \Rightarrow\ [O] = \dfrac{k_1[O_3]}{k_2[O_2] + k_3[O_3]} \\ \dfrac{d[O_3]}{dt} = -v_1 + v_2 - v_3 = -(v_2 + v_3) + v_2 - v_3 = -2v_3 \\ v = -\dfrac{1}{2}\dfrac{d[O_3]}{dt} = v_3 = k_3[O][O_3] = \dfrac{k_1 k_3[O_3]^2}{k_2[O_2] + k_3[O_3]} \end{cases}$$

Part H: **[11 marks]** At 44 °C, a solution of $AlCl_3$ is separated by a membrane. Outside the cell, a double-charged protein ion (whose couter ion is either Al^{3+} or Cl^-) is also present. The membrane is permeable to everything in the system except for the protein ion. The equilibrium concentrations of Cl^- inside and outside the cell are 0.45 M and 0.15 M, respectively. (**Note**: 0 °C = 273.15 K)

(a) [4 marks] Calculate the equilibrium concentrations of Al^{3+} inside and outside the cell.

$$\text{(a)} \begin{cases} \text{inside charge balance: } [\mathrm{Cl}^-]_{\mathrm{in}} = 3[\mathrm{Al}^{3+}]_{\mathrm{in}} \\ [\mathrm{Al}^{3+}]_{\mathrm{in}} = \dfrac{[\mathrm{Cl}^-]_{\mathrm{in}}}{3} = 0.15 \text{ M} \\ \text{Donnan equilibrium condition: } [\mathrm{Al}^{3+}]_{\mathrm{in}} \cdot [\mathrm{Cl}^-]_{\mathrm{in}}^3 = [\mathrm{Al}^{3+}]_{\mathrm{out}} \cdot [\mathrm{Cl}^-]_{\mathrm{out}}^3 \\ [\mathrm{Al}^{3+}]_{\mathrm{out}} = [\mathrm{Al}^{3+}]_{\mathrm{in}} \left(\dfrac{[\mathrm{Cl}^-]_{\mathrm{in}}}{[\mathrm{Cl}^-]_{\mathrm{out}}} \right)^3 = 0.15 \times \left(\dfrac{0.45}{0.15} \right)^3 = 4.05 \text{ M} \end{cases}$$

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

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

$$\text{(b)} \begin{cases} [\mathrm{Al}^{3+}]_{\mathrm{out}} > [\mathrm{Cl}^-]_{\mathrm{out}} \;\Rightarrow\; \text{outside charge balance} \\ \text{The protein ion has to be negatively charged} \end{cases}$$

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

$$\text{(c)} \begin{cases} \text{outside charge balance: } [\mathrm{Cl}^-]_{\mathrm{out}} + 2[\mathrm{Pr}^{2-}]_{\mathrm{out}} = 3[\mathrm{Al}^{3+}]_{\mathrm{out}} \\ [\mathrm{Pr}^{2-}]_{\mathrm{out}} = \dfrac{3[\mathrm{Al}^{3+}]_{\mathrm{out}} - [\mathrm{Cl}^-]_{\mathrm{out}}}{2} = \dfrac{3 \times 4.05 - 0.15}{2} = 6 \text{ M} \end{cases}$$

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

$$\text{(d)} \begin{cases} \varepsilon = -\dfrac{RT}{z_i F} \ln\left(\dfrac{[i]_R}{[i]_L} \right) \\ \text{using } \mathrm{Cl}^- : \; \varepsilon = -\dfrac{8.314 \times 317.15}{-1 \times 96485} \ln\left(\dfrac{0.15}{0.45} \right) = -0.03 \text{ V} \\ \text{using } \mathrm{Al}^{3+} : \; \varepsilon = -\dfrac{8.314 \times 317.15}{3 \times 96485} \ln\left(\dfrac{4.05}{0.15} \right) = -0.03 \text{ V} \end{cases}$$

(e) [2 marks] Calculate the osmotic pressure difference (in unit **atm**) across the cell membrane after the equilibrium is reached.

$$\text{(e)} \begin{cases} \Delta c = \left([\mathrm{Al}^{3+}]_{\mathrm{out}} + [\mathrm{Cl}^-]_{\mathrm{out}} + [\mathrm{Pr}^{2-}]_{\mathrm{out}} \right) - \left([\mathrm{Al}^{3+}]_{\mathrm{in}} + [\mathrm{Cl}^-]_{\mathrm{in}} \right) \\ \Delta c = (4.05 + 0.15 + 6) - (0.15 + 0.45) = 9.6 \text{ M} \\ \Delta \Pi = \Delta c \cdot RT = 9.6 \times 0.08206 \times 317.15 = 249.8 \text{ atm } (2.53 \times 10^7 \text{ Pa}) \end{cases}$$

Part I: **[10 marks]** We know the following standard reduction potentials, at 25 °C (**Note**: 0 °C = 273.15 K):

$Au^{3+}(aq) + 2\,e^- \rightarrow Au^+(aq)$ $\varepsilon_1° = 1.36$ V
$Au^+(aq) + e^- \rightarrow Au(s)$ $\varepsilon_2° = 1.83$ V

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

Anode	$Au^+(aq) \rightarrow Au^{3+}(aq) + 2\,e^-$
Cathode	$Au^+(aq) + e^- \rightarrow Au(s)$
Total Cell	$3\,Au^+(aq) \rightarrow 2\,Au(s) + Au^{3+}(aq)$

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

$$\text{(b)}\ \begin{cases} \varepsilon^0 = \varepsilon_2^0 - \varepsilon_1^0 = 1.83 - 1.36 = 0.47\ \text{V} \\ \Delta G^0 = -nF\varepsilon^0 = -2\times 96485\times 0.47 = -90695.9\ \text{J}\ \ (-90.7\ \text{kJ}) \end{cases}$$

(c) [2 marks] If $[Au^{3+}] = 1.0$ M, at what concentration of $Au^+(aq)$ would the cell become nonspontaneous?

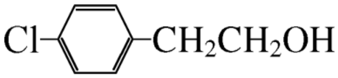
$$\text{(c)}\ \begin{cases} \varepsilon = \varepsilon^0 - \dfrac{RT}{nF}\ln Q \le 0 \ \Rightarrow\ \ln Q \ge \dfrac{nF\varepsilon^0}{RT} = 36.59 \\ Q = \dfrac{[Au^{3+}]}{[Au^+]^3} \ge e^{36.59} \ \Rightarrow\ [Au^+] \le \left(\dfrac{[Au^{3+}]}{e^{36.59}}\right)^{\frac{1}{3}} \\ [Au^+] \le e^{-12.2}\ \text{M}\ \ (5.05\times 10^{-6}\ \text{M}) \end{cases}$$

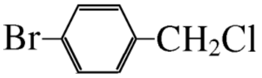
(d) [2 marks] Calculate emf $\varepsilon_3°$ for the half-cell reaction: $Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$

$$\text{(d)}\ \begin{cases} \Delta G_1^0 = -n_1F\varepsilon_1^0 = -2F\varepsilon_1^0 \\ \Delta G_2^0 = -n_2F\varepsilon_2^0 = -F\varepsilon_2^0 \\ \Delta G_3^0 = -n_3F\varepsilon_3^0 = -3F\varepsilon_3^0 \\ \Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0 \ \Rightarrow\ -3F\varepsilon_3^0 = -2F\varepsilon_1^0 - F\varepsilon_2^0 \\ \varepsilon_3^0 = \dfrac{2\varepsilon_1^0 + \varepsilon_2^0}{3} = \dfrac{2\times 1.36 + 1.83}{3} = 1.52\ \text{V} \end{cases}$$

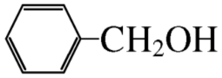
$$\text{OR:}\ \begin{cases} \text{Anode:} & Au(s) \rightarrow Au^{3+}(aq) + 3e^- & -\varepsilon_3^0 & \Delta G_3^0 = 3F\varepsilon_3^0 \\ \text{Cathode:} & 3Au^+(aq) + 3e^- \rightarrow 3Au(s) & +\varepsilon_2^0 & \Delta G_2^0 = -3F\varepsilon_2^0 \\ \text{Total Cell:} & 3Au^+(aq) \rightarrow 2Au(s) + Au^{3+}(aq) & +\varepsilon^0 & \Delta G^0 = -2F\varepsilon^0 \\ \multicolumn{4}{l}{\Delta G^0 = \Delta G_3^0 + \Delta G_2^0 \ \Rightarrow\ \varepsilon_3^0 = \varepsilon_2^0 - \dfrac{2\varepsilon^0}{3} = 1.83 - \dfrac{2\times 0.47}{3} = 1.52\ \text{V}} \end{cases}$$

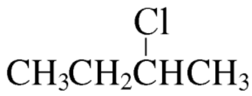
Part J: [6 marks] Assign the correct molecular formula (or structure) to each of the following ^{1}H NMR spectrum. Fill in the box using the appropriate number corresponding to a particular molecule, *e.g.*, $\boxed{8}$. There is only one correct formula (or structure) for each NMR spectrum. Note that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

1)


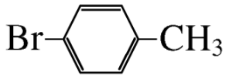
2)


3) $CH_3CH_2CH_3$

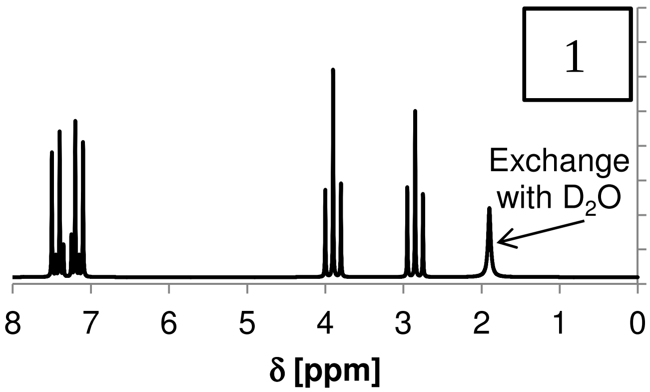
4)


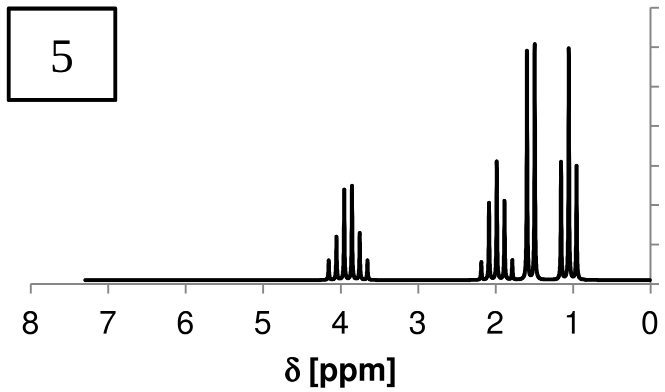
5)

$CH_3CH_2CH(Cl)CH_3$

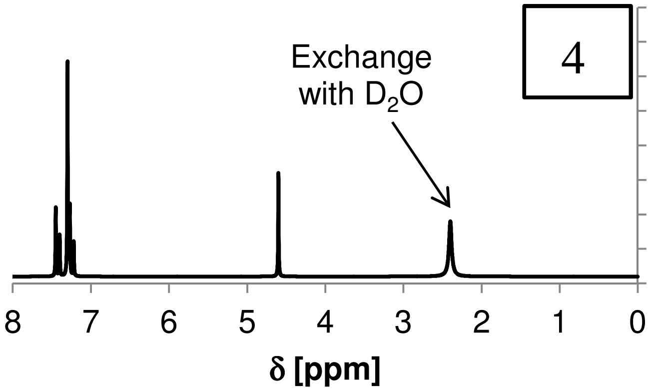
6) $Cl{-}CH_2CH(CH_3)_2$

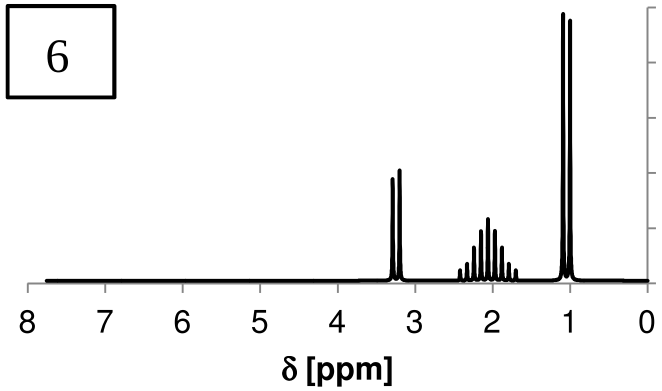
7)


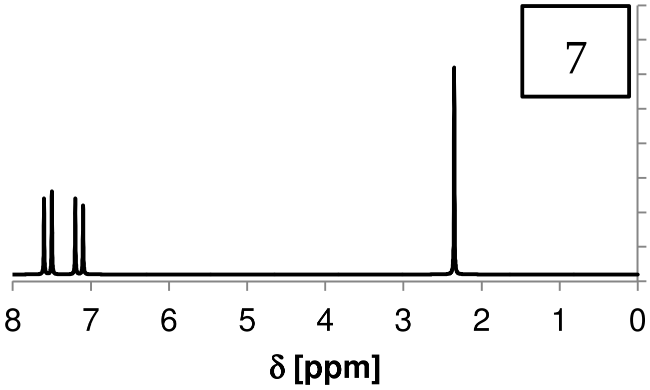
8) $(CH_3)_2CH{-}Cl$

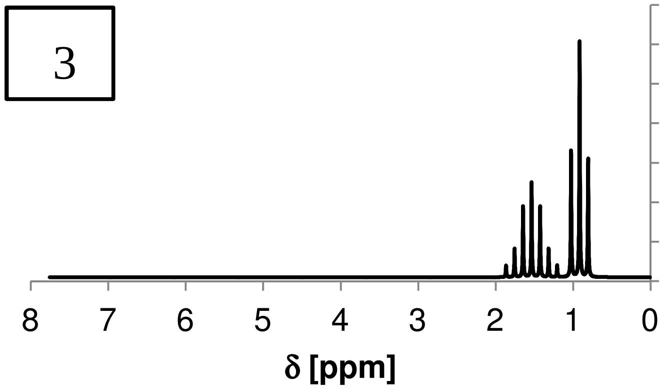




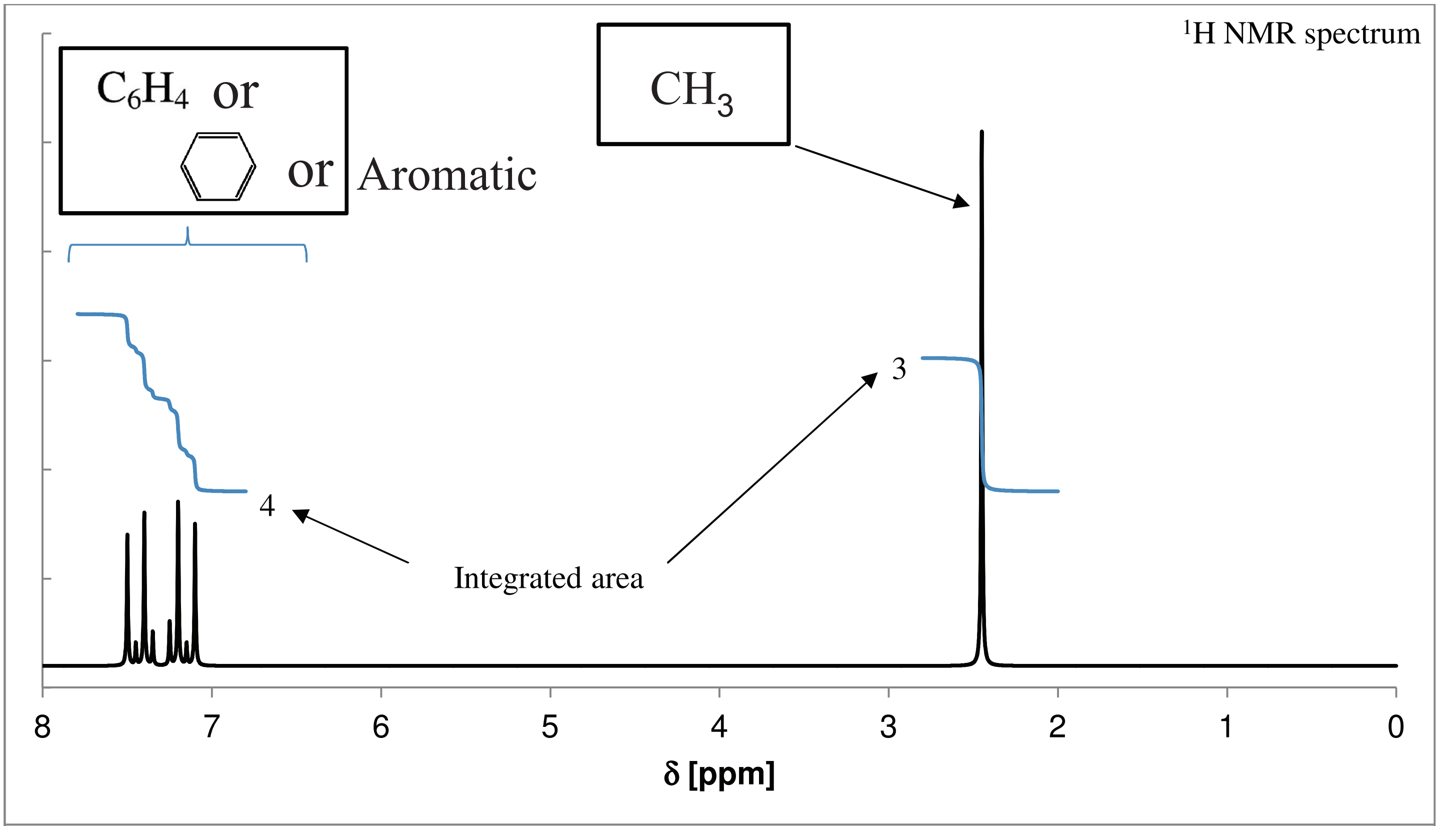


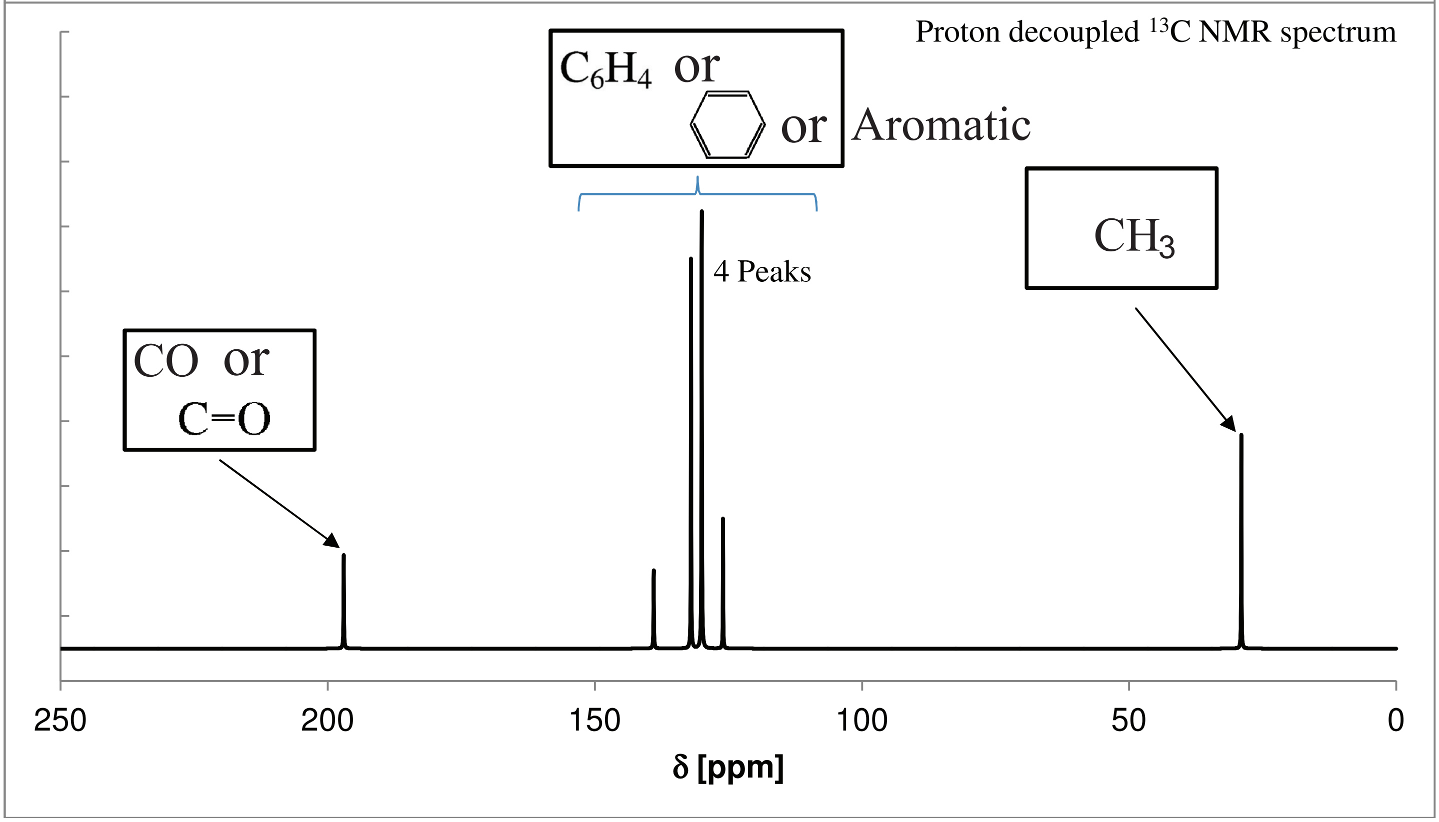


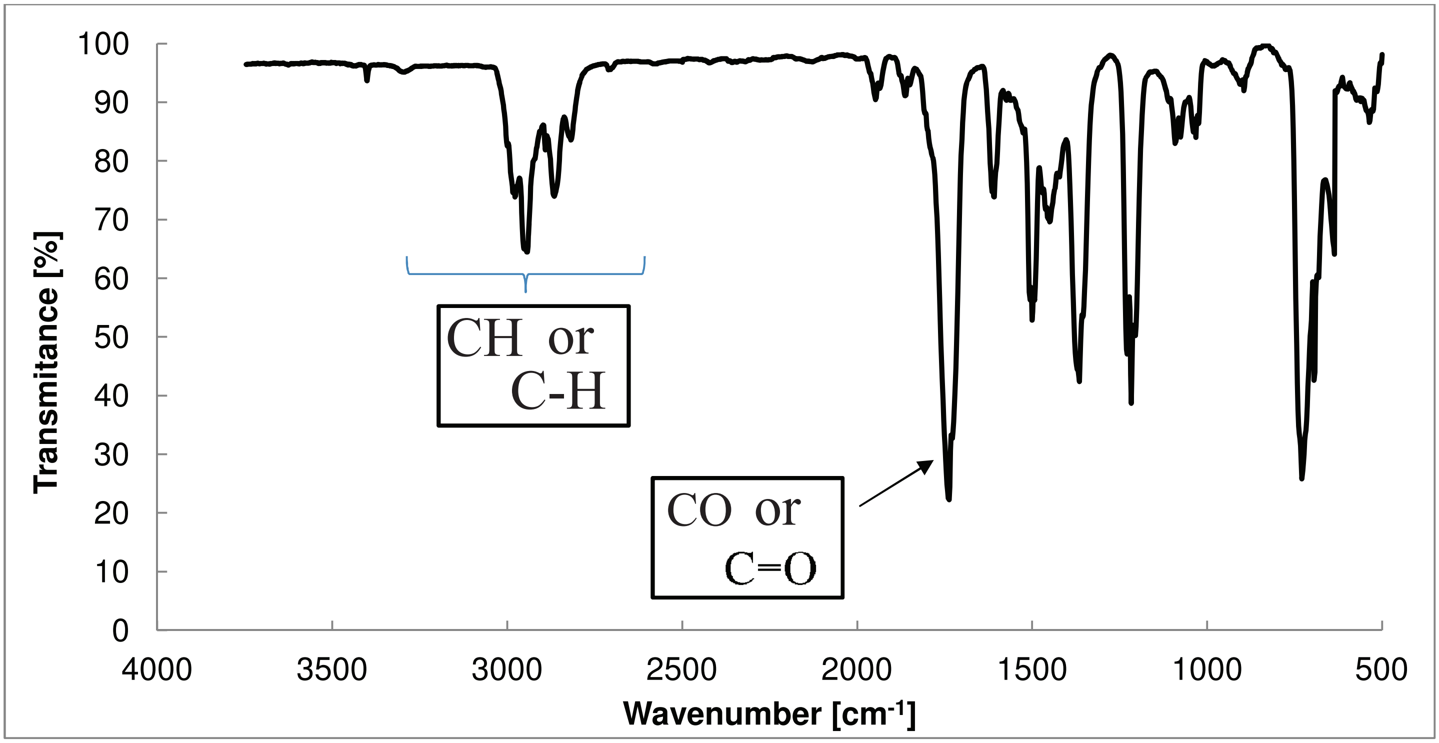


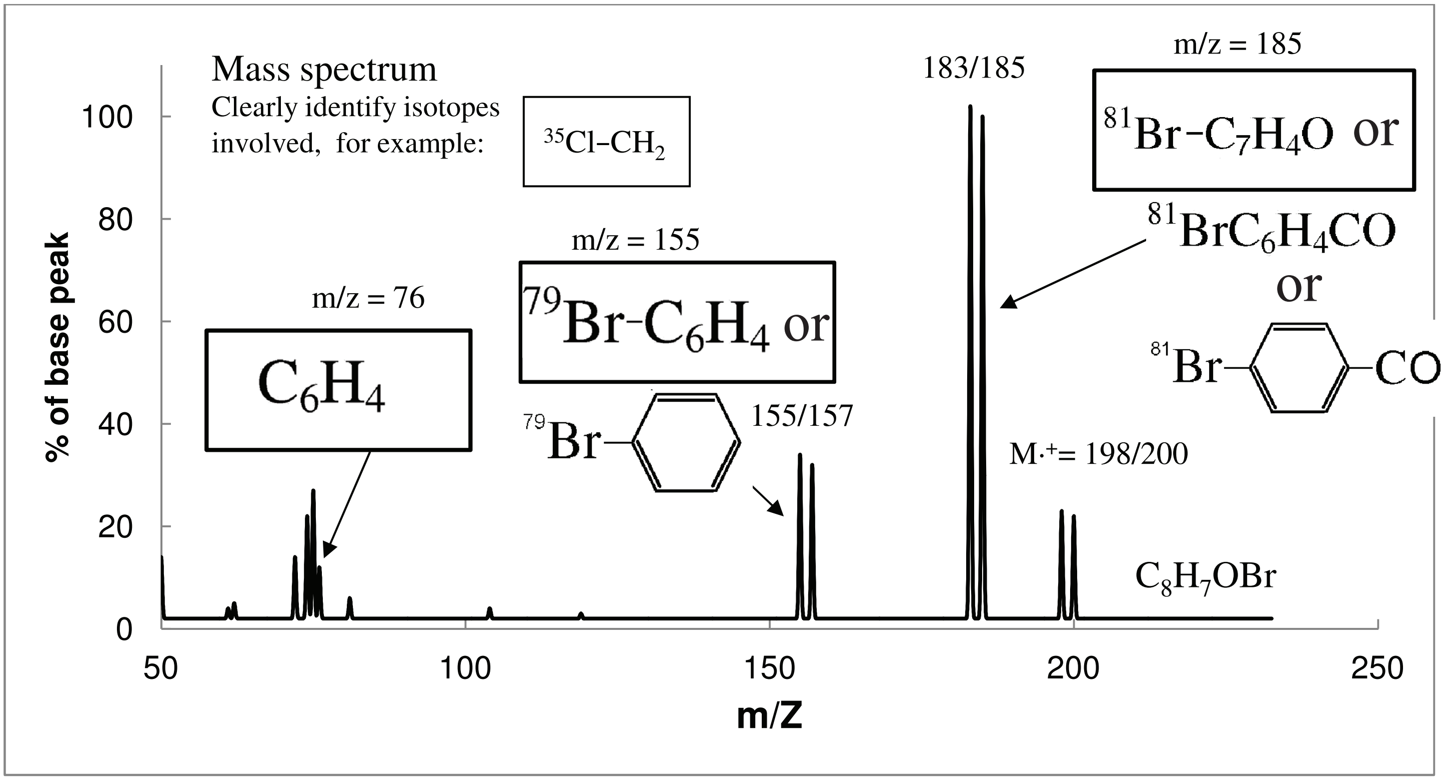


Part K: [11 marks] The following spectra were collected for a compound of formula C_8H_7OBr. Fill the boxes in each spectrum to show which chemical moiety (*e.g.*, $-CH_3$, $-CH_2-$, *etc.*) gives rise to the peaks indicated by bracket or arrow. Identify the compound by drawing its structure in the big empty box on the next page.









UV Spectrum:
λ_{max} 258 nm (log ε = 4.2)
Solvent ethanol

Draw the structure of the molecule in the box: