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.

Name: ______________________ (print, surname first)

Student number: ______________________

Signature: ______________________

Lecture Section: ______________________

University of British Columbia
CHEM 205 Final Examination
12 April 2013, 12:00−2:30 PM

Time: 2 hours 30 minutes
Answer all questions
NON-PROGRAMMABLE NON-GRAPHING CALCULATORS ARE PERMITTED

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	15	
Part B	10	
Part C	6	
Part D	12	
Part E	8	
Part F	8	
Part G	11	
Part H	10	
Part I	6	
Part J	5	
Part K	9	
Total	100	

Part A: [15 marks] Circle in the **BEST** answer for each of the following questions.

1. [1 mark] If the order of a chemical reaction 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] 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) $C_A = -2\,v_{mean}$

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 preceed.

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 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 or the equilibrium constant.

7. [1 mark] The following statement for chemical equilibrium apply 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) 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] 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 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) We cannot tell from the given information whether a catalyst is present.

10. [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) the formula $\Delta G = w'$ should be used all the time.

11. [1 mark] If a **proposed** exothermic chemical reaction will also descrease the entropy of the system, this chemical reaction will proceed spontaneously:

1) forward 2) backward 3) in equilibrium 4) canot be determined

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

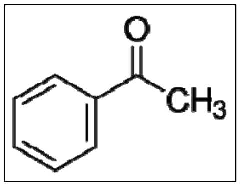
1) Infrared light is in red color.
2) Ultraviolet light has extremely violet color.
3) X-ray is in black and white.
4) Visible light is always white unless it is in the rainbows.
5) None of the above.

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

1) in the ^1H 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 ^1H 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.



15. [1 mark] At the same temperature and pressure, the equilibrium constant of the first reaction

$2\,A(g) + 2\,B(g) \leftrightarrows D(g)$ is K_1, and the equilibrium constant of the second reaction

$\frac{1}{2}D(g) \leftrightarrows A(g) + B(g)$ is K_2, which of the following 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

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 on below)

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

Part C: [6 marks] The decomposition of CH_3Br is a first-order reaction with an activation energy: $E_a = 229.3$ kJ. 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.

(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 D: [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 E: [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 (Pa)	1333	20270

(a) [6 marks] Calculate ΔG, ΔH, and ΔS for the vaporization of SO_2 at 6.3 °C and 20270 Pa.
(**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 700000 Pa. 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 F: **[8 marks]** The gas phase reaction: $SF_4(g) + F_2(g) \leftrightarrows SF_6(g)$ has a standard Gibbs energy of reaction of −373.8 kJ/mol at 25 °C. The standard Gibbs energy of formation of $SF_6(g)$ amounts to −1105.1 kJ/mol. (**Note**: 0 °C = 273.15 K)

(a) [2 marks] Calculate the equilibrium constant.

(b) [2 marks] Calculate the standard Gibbs energy of formation of $SF_4(g)$.

(c) [4 marks] The standard entropies of the different gases are given in the following table:

	$SF_6(g)$	$SF_4(g)$	$F_2(g)$
S^0 [J K^{-1} mol^{-1}]	292	293	203

Calculate the standard enthalpy of reaction.

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

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

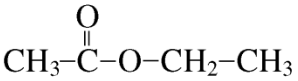
Anode	
Cathode	
Total Cell	

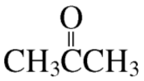
(b) [3 marks] Calculate emf $\varepsilon°$ and $\Delta G°$ for the total cell reaction.

(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: $Au^{3+}(aq) + 3\,e^{-} \rightarrow Au(s)$

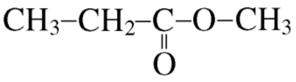
Part I: [6 marks] Assign the correct molecular formula (or structure) to each of the following ^{1}H NMR spectrum. Fill in the box using the appropriate number corresponding to a particular molecule, *e.g.*, $\boxed{8}$. There is only one correct formula (or structure) for each NMR spectrum. Note that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

1)  $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

4)  $CH_3\overset{\overset{O}{\|}}{C}CH_3$

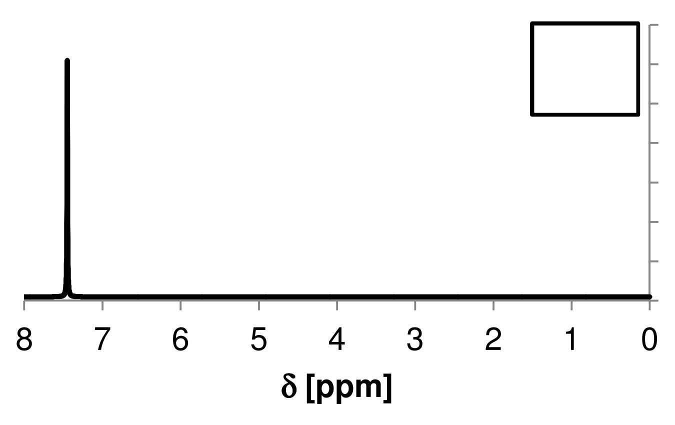
2) C_6H_6

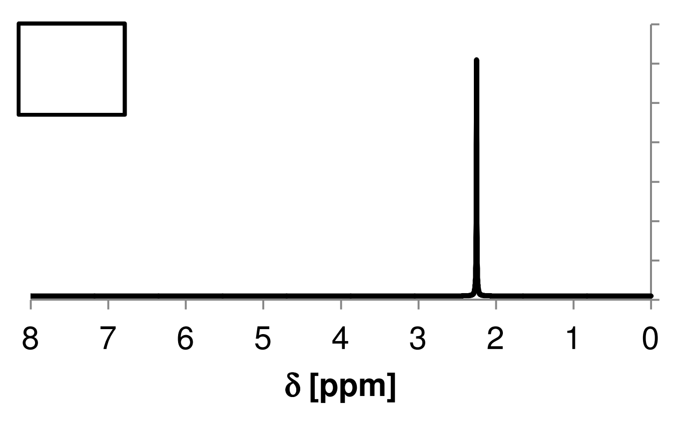
5) $Br-C_6H_4-CH_3$

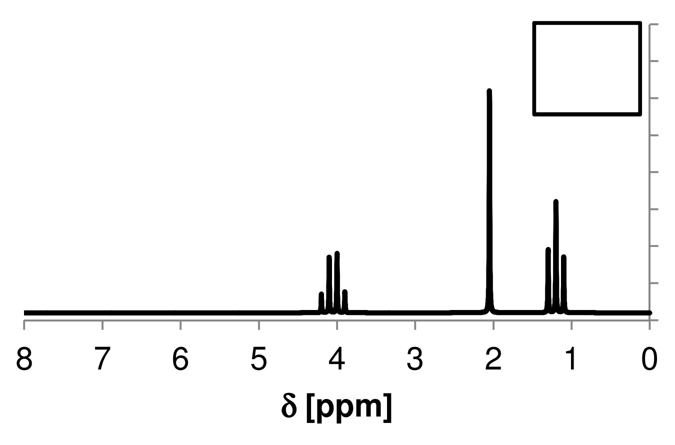
3)  $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_3$

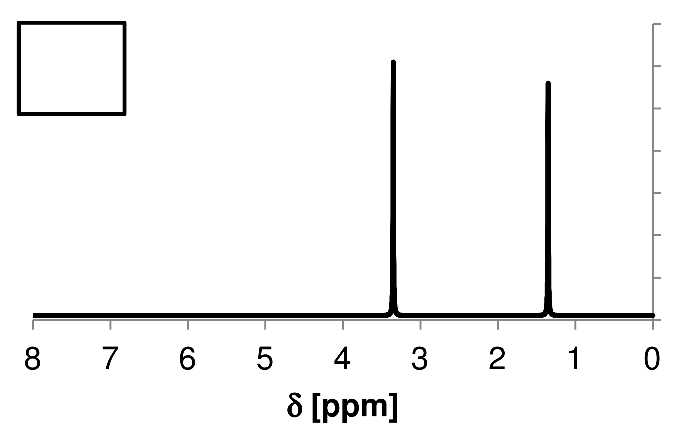
6) $(CH_3)_2CH-OH$

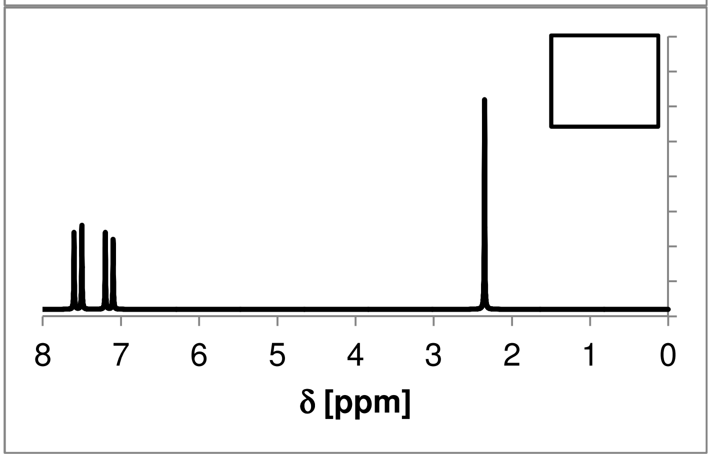
7) $(CH_3)_2C(OCH_3)_2$

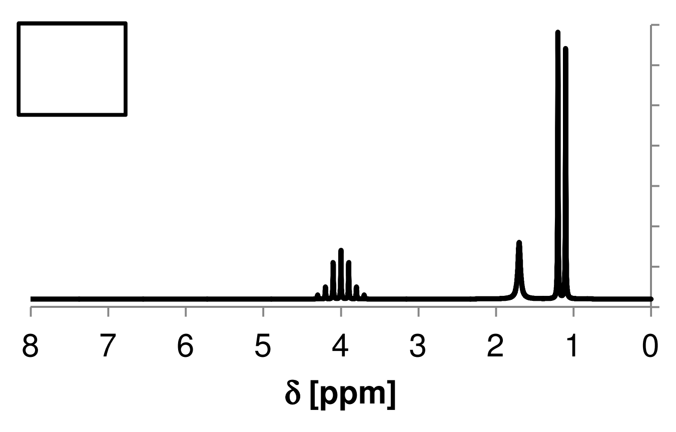




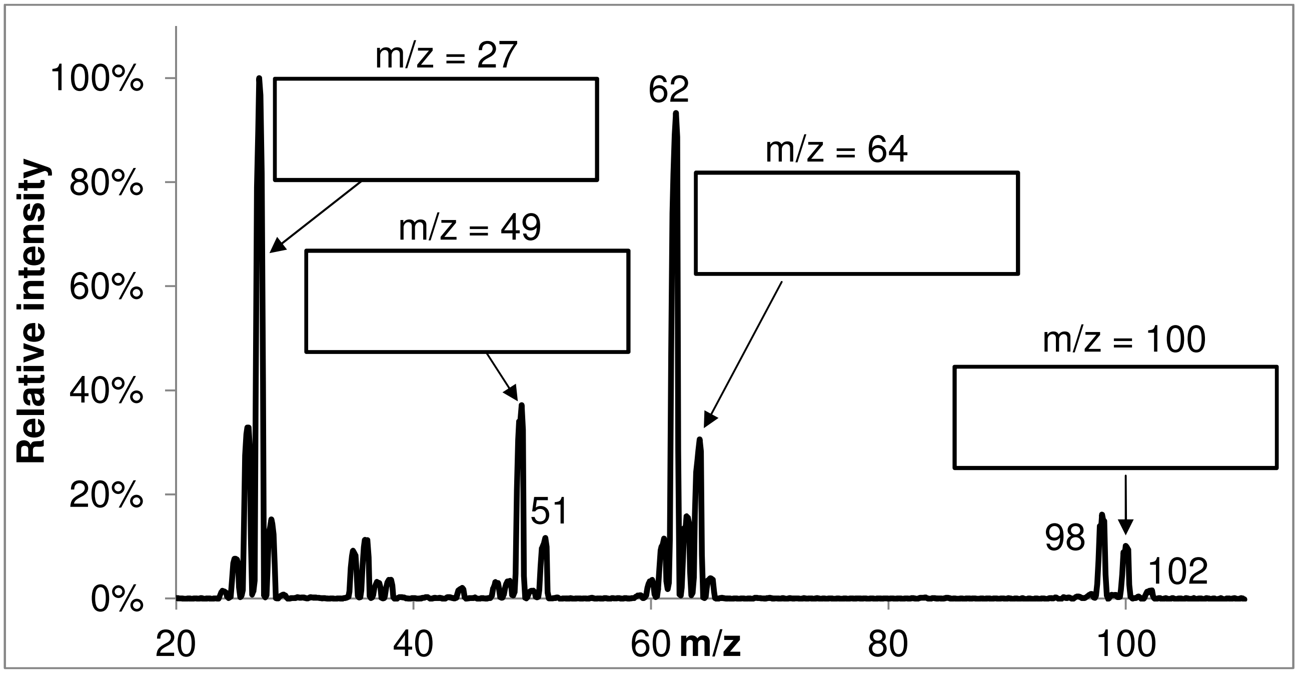








Part J: [5 marks] An undergraduate chemistry student collected a mass spectrum:

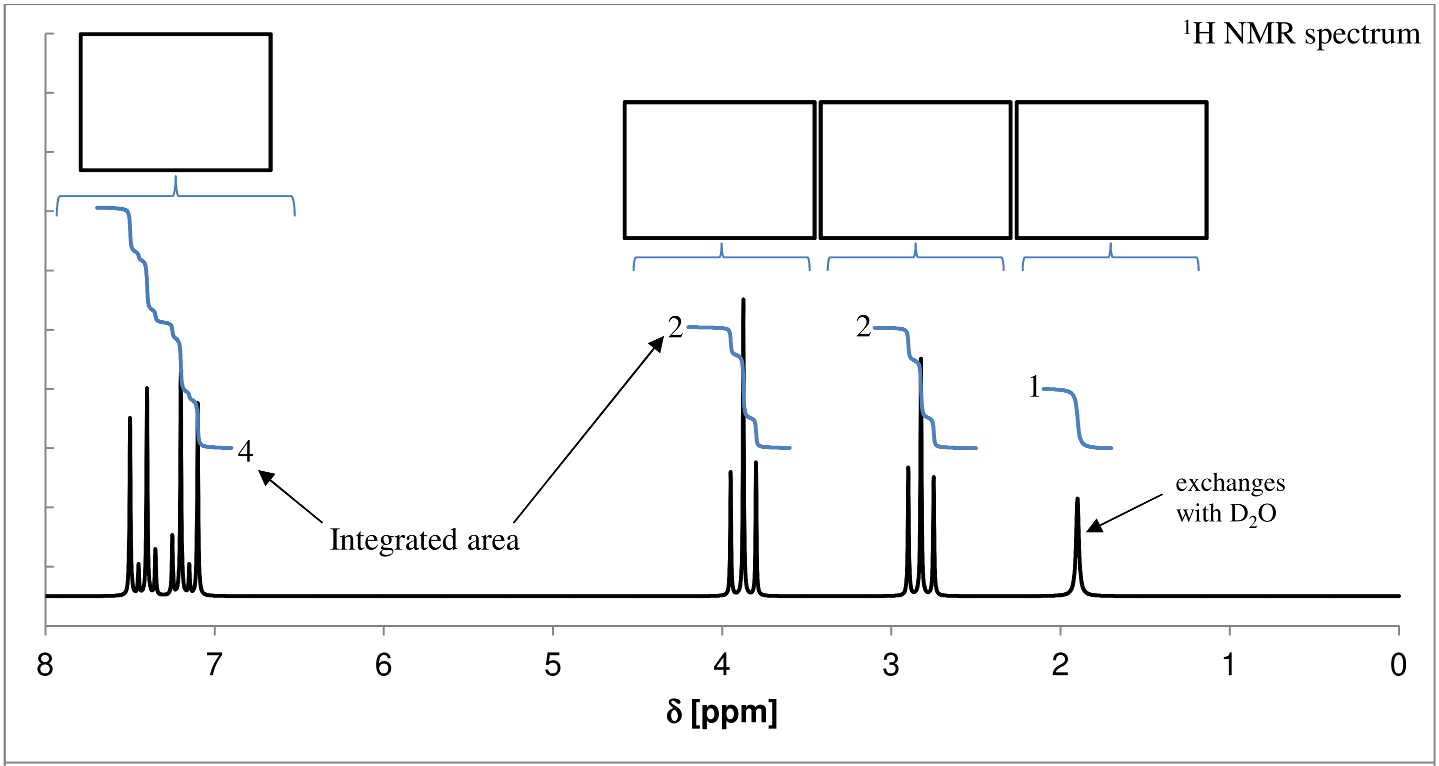


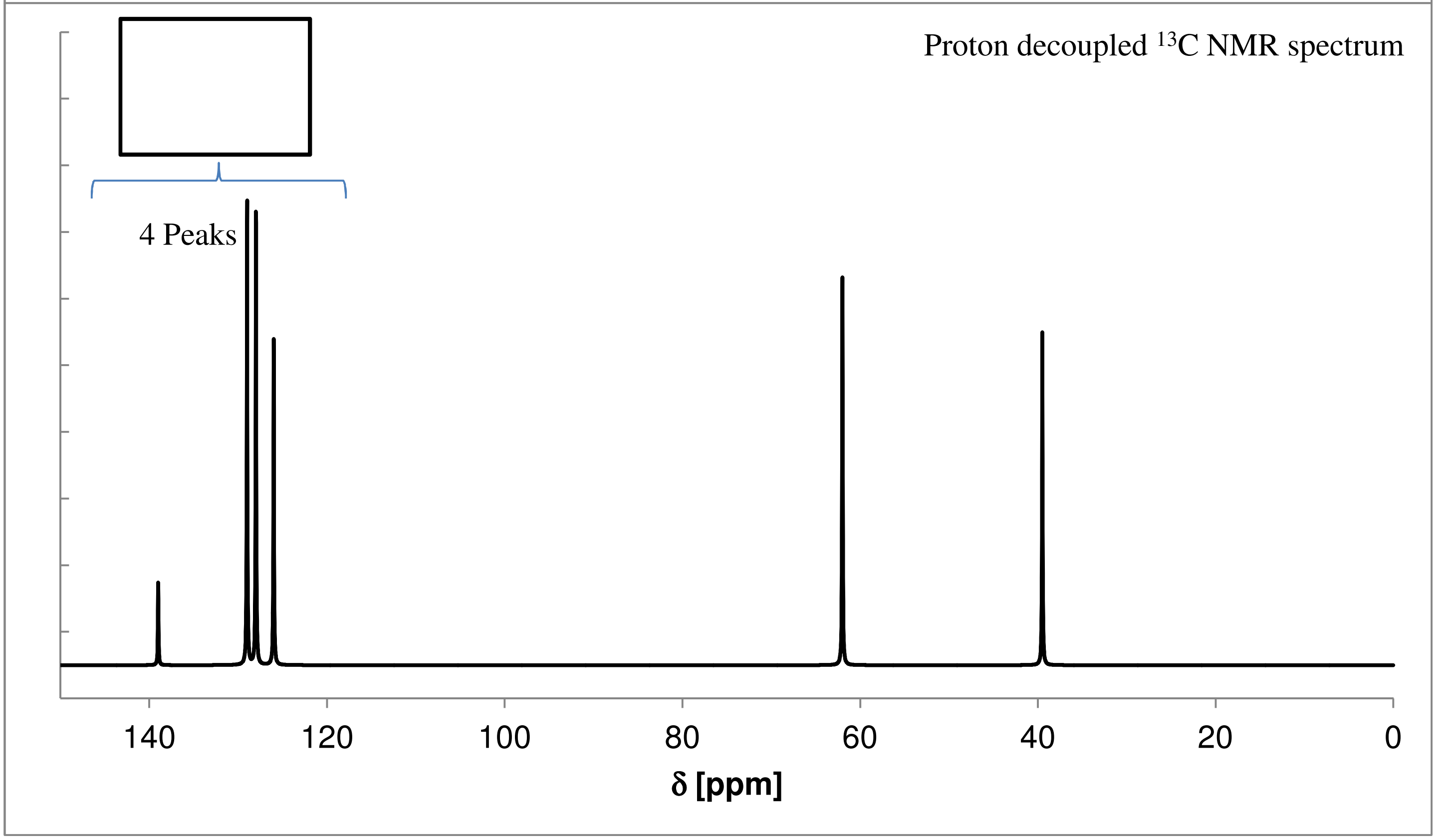
(a) [1 mark] Please identify which of the following molecule is responsible for the above mass spectrum? (circle one below)

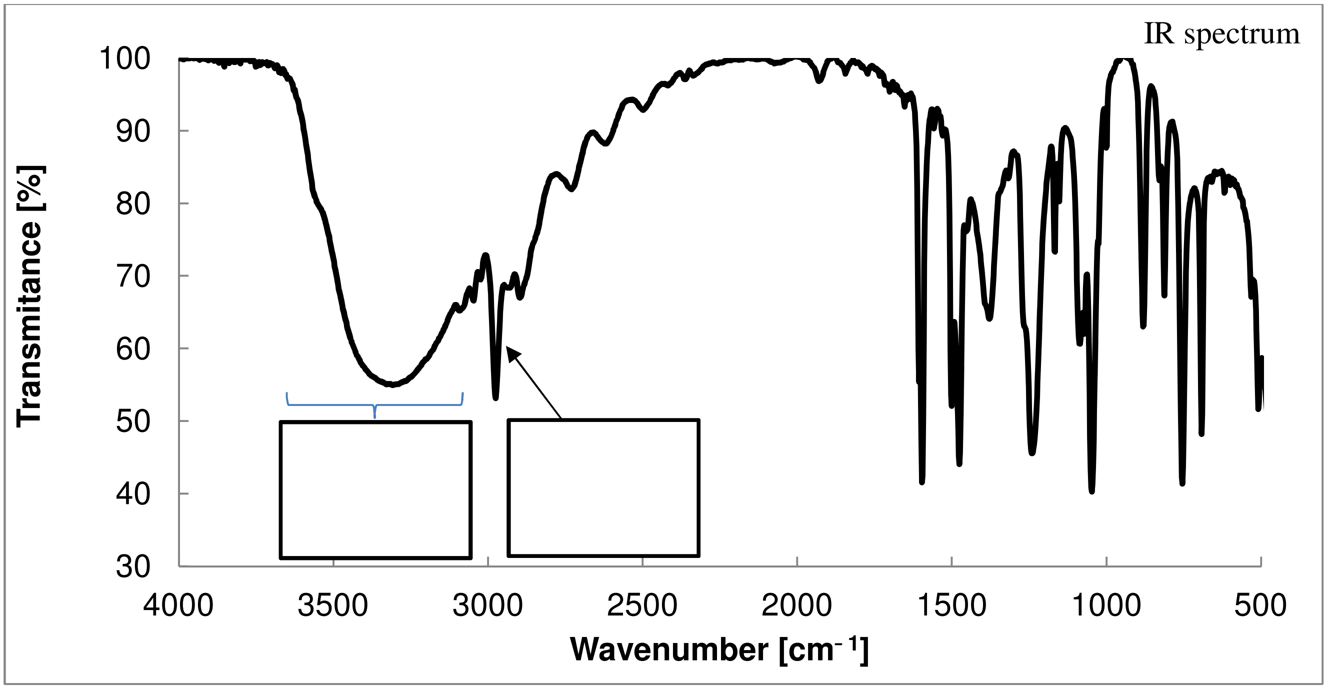
1) CH_2Cl_2
2) $CHCl_3$
3) C_2H_5Cl
4) $C_2H_4Cl_2$
5) CH_3Cl
6) $C_2H_3Cl_3$

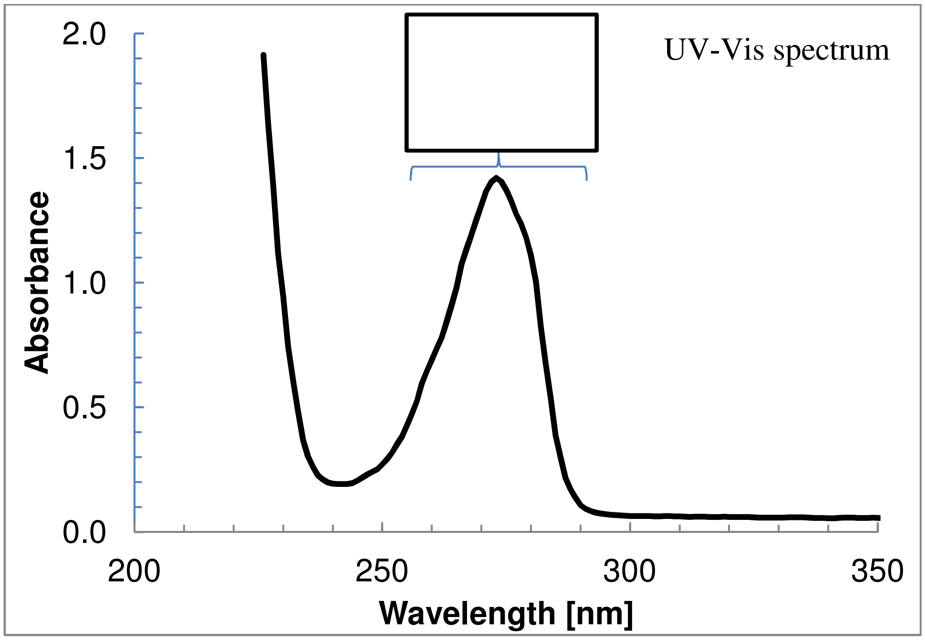
(b) [4 marks] Then write the chemical formula **of the fragment** (of your chosen molecule) responsible for each labeled signal inside the boxes in the above mass spectrum. Be sure to clearly identify isotopes involved, for example: $\boxed{^{81}Br^{79}BrC_3H_6}$

Part K: [9 marks] The following spectra were collected for a compound of formula C_8H_9OCl. 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.









Draw the structure of the molecule in the box below:

SOME FAMILIAR EQUATIONS and CONSTANTS:

NOTE: conditions to which they apply are NOT specified here.

R = 8.314 J K^{-1} mol^{-1} = 0.08206 L atm K^{-1} mol^{-1}
$k = 1.3807 \times 10^{-23}$ JK^{-1}
$e = 1.602 \times 10^{-19}$ C
$N_A = 6.0221 \times 10^{23}$ mol^{-1}
$F = eN_A$ = 96485 C mol^{-1}
$c = 2.998 \times 10^{8}$ m/s
$h = 6.626 \times 10^{-34}$ J s
1 atm = 101325 Pa

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

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

$$dw = -p_{ex}\,dV$$

$$w = -p_{ex}\,(V_2 - V_1)$$

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

$$dq = C\,dT$$

$$nC_{V,m} = (dq_V / dT)$$

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

$$H = U + pV$$

$$nC_{p,m} = (dq_p / dT)$$

$$(\Delta H)_p = q_p = \int_{T_1}^{T_2} nC_{p,m}\,dT$$

$$C_{V.m} = \frac{3}{2}R \qquad C_{p,m} = \frac{5}{2}R$$

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

$$S = k\ln W$$

$$\Delta S = S_2 - S_1 = \int_{state1}^{state2} (dq_{rev}/T)$$

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

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

$$\Delta S_{univ} = \Delta S + \Delta S_{surr}$$

$$\ln\frac{p_2}{p_1} = -\frac{\Delta_{vap}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$G = H - TS$$

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

$$\Delta_r G = \Delta_r G^0 + RT\ln(Q)$$

$$E = -\frac{\Delta_r G^0}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$
$$= E^0 - \frac{R \cdot T}{n \cdot F} \cdot \ln(Q)$$

$$\Delta T_b = T_{b,mix} - T_{b,pure} \approx K_b b_B = K_b m_B$$

$$\Delta T_f = T_{f,mix} - T_{f,pure} \approx -K_f b_B = -K_c m_B$$

$$\Pi = c_B\,RT$$

$$\varepsilon \approx -\frac{RT}{z_i F}\ln\left(\frac{[i]_R}{[i]_L}\right)$$

$$\Delta\Pi = \Delta cRT$$

$$c = \lambda\,\nu$$

$$\Delta E = h\,\nu = h\,c/\lambda$$

$$T = I / I_0$$

$$A = \log_{10}(I_0 / I) = \varepsilon\,c\,l$$

$$E_{vib} = \hbar\sqrt{\frac{k}{\mu}}\left(v + \frac{1}{2}\right)$$

$$[A] = [A]_0 - k\,t \quad and \quad t_{1/2} = [A]_0/(2k)$$

$$\ln\left(\frac{[A]}{[A]_0}\right) = -k\,t \quad and \quad t_{1/2} = (\ln 2)/k$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k\,t \quad and \quad t_{1/2} = \frac{1}{k\,[A]_0}$$

$$k = A\exp(-E_a/(RT))$$

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

$$\nu = \frac{\nu_{\max}[S]}{[S] + K_M}$$

USEFUL SPECTROSCOPIC DATA

IR MODES OF VIBRATIONAL FREQUENCY

VIBRATION	**ν (cm^{-1})**
C-C stretch,bend	700-1250
C-H stretch	2850-2960 (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)

UV-VISIBLE ABSORPTION BANDS

CHROMOPHORE	**λ_{max} (nm)**
C=O (carbonyl ketones and aldehydes)	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)

SELECTED ISOTOPES AND THEIR MASSES

ISOTOPE	**NATURAL ABUNDANCE (%)**	**MASS**
^{1}H	99.98	1.00783
^{12}C	98.9	12.0000
^{13}C	1.1	13.00336
^{14}N	99.6	14.0031
^{16}O	99.8	15.9949
^{19}F	100.0	18.99840
^{35}Cl	75.8	34.9689
^{37}Cl	24.2	36.9659
^{79}Br	50.7	78.9183
^{81}Br	49.3	80.9163

COMMON FRAGMENTS AND THEIR MASSES

FRAGMENT	**MASS**
CH_3	15
CH_2CH_3	29
HC(=O)	29
$HOCH_2$	31
$CH_3C(=O)$	43
HOC(=O)	45

NMR PROTON CHEMICAL SHIFTS

TYPE OF PROTON	**Downfield Shift δ from TMS**
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
$ROCH_2R$	3.3-3.9
RCH_2OH	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

NMR ^{13}C CHEMICAL SHIFTS

GROUP	**^{13}C SHIFT RANGE (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
$O-CH_3$	50 - 60
$N-CH_3$	15 – 45
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

Part A: [15 marks] Circle in the **BEST** answer for each of the following questions.

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

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

2. [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) $C_A = -2\,v_{\text{mean}}$

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 preceed.

[✓ 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 of the dye molecule?

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

Q1	Q2	Q3	Q4	Q5
1	3	5	4	4

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 or the equilibrium constant.

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

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

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

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

[✓ 4) 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] 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:

$$\mathrm{Cl\cdot} + O_3 \rightarrow \mathrm{ClO\cdot} + O_2$$

$$O_3 + \mathrm{ClO\cdot} \rightarrow \mathrm{Cl\cdot} + 2\,O_2$$

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

10. [1 mark] To calculate the expansion work for a process,

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

2) the formula $\mathrm{d}w = -P_{\text{ex}}\,\mathrm{d}V$ can only be used for irreversible processes.

[✓ 3) the formula $\mathrm{d}w = -P_{\text{ex}}\,\mathrm{d}V$ always works under all conditions.]

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

5) the formula $\Delta G = w'$ should be used all the time.

Q6	Q7	Q8	Q9	Q10
1	4	3	4	3

11. [1 mark] If a **proposed** exothermic chemical reaction will also descrease the entropy of the system, this chemical reaction will proceed spontaneously:

1) forward 2) backward 3) in equilibrium [✓ 4) canot be determined]

12. [1 mark] Which of the following statement 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.

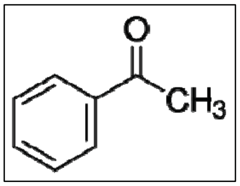
2) no more energy can be supplied because all reactants are used up.

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



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

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

15. [1 mark] At the same temperature and pressure, the equilibrium constant of the first reaction

$2\,A(g) + 2\,B(g) \leftrightarrows D(g)$ is K_1, and the equilibrium constant of the second reaction

$\frac{1}{2}D(g) \leftrightarrows A(g) + B(g)$ is K_2, which of the following 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

Q11	Q12	Q13	Q14	Q15
4	5	4	3	4

Part B: [10 marks] Three moles of an ideal gas undergoes an isothermal process at $T = 25\ ^\circ\text{C}$, 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**: $0\ ^\circ\text{C} = 273.15\ \text{K}$)

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

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

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

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

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

(c) [1 mark] Is the process spontaneous? (circle on below)

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

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

Part C: [6 marks] The decomposition of CH_3Br is a first-order reaction with an activation energy: E_a = 229.3 kJ. 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.

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

(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.

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

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

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

Part D: [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	$v_3 =$

$$\text{(a)}\ \begin{cases} v_1 = k_1[\mathrm{O_3}] \\ v_2 = k_2[\mathrm{O}][\mathrm{O_2}] \\ v_3 = k_3[\mathrm{O}][\mathrm{O_3}] \end{cases}$$

(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** of the formation of O_2 using v_1, v_2, and v_3:

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

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

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

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

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

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

$$v = -\frac{1}{2}\frac{d[\mathrm{O_3}]}{dt} = \frac{k_1k_3[\mathrm{O_3}]^2}{k_2[\mathrm{O_2}] + k_3[\mathrm{O_3}]}$$

$$\text{(e)}\ \begin{cases} \dfrac{d[\mathrm{O}]}{dt} = 0 \;\Rightarrow\; v_1 = v_2 + v_3 \;\Rightarrow\; [\mathrm{O}] = \dfrac{k_1[\mathrm{O_3}]}{k_2[\mathrm{O_2}] + k_3[\mathrm{O_3}]} \\ \dfrac{d[\mathrm{O_3}]}{dt} = -v_1 + v_2 - v_3 = -(v_2 + v_3) + v_2 - v_3 = -2v_3 \\ v = -\dfrac{1}{2}\dfrac{d[\mathrm{O_3}]}{dt} = v_3 = k_3[\mathrm{O}][\mathrm{O_3}] = \dfrac{k_1k_3[\mathrm{O_3}]^2}{k_2[\mathrm{O_2}] + k_3[\mathrm{O_3}]} \end{cases}$$

Part E: [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 (Pa)	1333	20270

(a) [6 marks] Calculate ΔG, ΔH, and ΔS for the vaporization of SO_2 at 6.3 °C and 20270 Pa.
(**Note**: 0 °C = 273.15 K)

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

(b) [2 marks] Assume that some liquid SO_2 is contained in a glass cylinder which breaks at a pressure of 700000 Pa. 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.**

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

Part F: **[8 marks]** The gas phase reaction: $SF_4(g) + F_2(g) \leftrightarrows SF_6(g)$ has a standard Gibbs energy of reaction of −373.8 kJ/mol at 25 °C. The standard Gibbs energy of formation of $SF_6(g)$ amounts to −1105.1 kJ/mol. (**Note**: 0 °C = 273.15 K)

(a) [2 marks] Calculate the equilibrium constant.

$$\text{(a)} \begin{cases} \Delta G^0 = -RT \cdot \ln K \ \Rightarrow \ \ln K = \dfrac{-\Delta G^0}{RT} = \dfrac{373.8\times 10^3}{8.314\times 298.15} = 150.8 \\ K = e^{150.8} = 3.1\times 10^{65} \end{cases}$$

(b) [2 marks] Calculate the standard Gibbs energy of formation of $SF_4(g)$.

$$\text{(b)} \begin{cases} \Delta G^0 = \Delta G_f^0(\mathrm{SF_6}) - \Delta G_f^0(\mathrm{SF_4}) \ \Rightarrow \ \Delta G_f^0(\mathrm{SF_4}) = \Delta G_f^0(\mathrm{SF_6}) - \Delta G^0 \\ \Delta G_f^0(\mathrm{SF_4}) = -1105.1 + 373.8 = -731.3 \ \text{kJ/mol} \end{cases}$$

(c) [4 marks] The standard entropies of the different gases are given in the following table:

	$SF_6(g)$	$SF_4(g)$	$F_2(g)$
S^0 [J K^{-1} mol^{-1}]	292	293	203

Calculate the standard enthalpy of reaction.

$$\text{(c)} \begin{cases} \Delta S^0 = S^0(\mathrm{SF_6}) - S^0(\mathrm{SF_4}) - S^0(\mathrm{F_2}) = 292 - (293 + 203) = -204 \ \text{J/K} \\ \Delta G^0 = \Delta H^0 - T\cdot\Delta S^0 \ \Rightarrow \ \Delta H^0 = \Delta G^0 + T\cdot\Delta S^0 \\ \Delta H^0 = -373.8 + 298.15\times(-204)\times 10^{-3} = -434.6 \ \text{kJ} \ (-435 \ \text{kJ}) \end{cases}$$

Part G: [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.

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

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

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

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

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

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

(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.

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

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

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

$$\mathrm{Au^{+}}(aq) + \mathrm{e^-} \rightarrow \mathrm{Au}(s) \qquad \varepsilon_2° = 1.83\ \mathrm{V}$$

(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	

$$\text{(a)}\ \begin{cases} \text{Anode:} & \mathrm{Au^+}(aq) \rightarrow \mathrm{Au^{3+}}(aq) + 2\mathrm{e^-} \\ \text{Cathode:} & \mathrm{Au^+}(aq) + \mathrm{e^-} \rightarrow \mathrm{Au}(s) \\ \text{Total Cell:} & 3\mathrm{Au^+}(aq) \rightarrow 2\mathrm{Au}(s) + \mathrm{Au^{3+}}(aq) \end{cases}$$

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

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

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

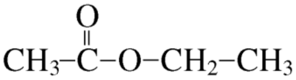
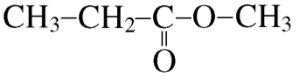
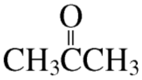
$$\text{(c)}\ \begin{cases} \varepsilon = \varepsilon^0 - \dfrac{RT}{nF}\ln Q \le 0 \ \Rightarrow\ \ln Q \ge \dfrac{nF\varepsilon^0}{RT} = 36.59 \\ Q = \dfrac{[\mathrm{Au^{3+}}]}{[\mathrm{Au^+}]^3} \ge e^{36.59} \ \Rightarrow\ [\mathrm{Au^+}] \le \left(\dfrac{[\mathrm{Au^{3+}}]}{e^{36.59}}\right)^{\frac{1}{3}}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

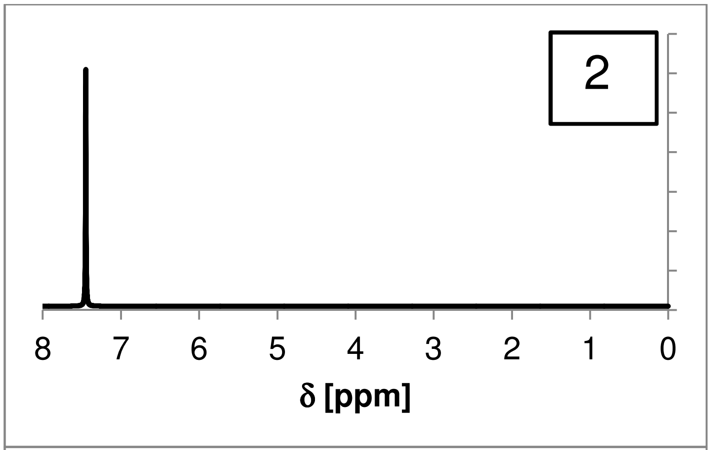
(d) [2 marks] Calculate emf $\varepsilon_3°$ for the half-cell reaction: $\mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \rightarrow \mathrm{Au}(s)$

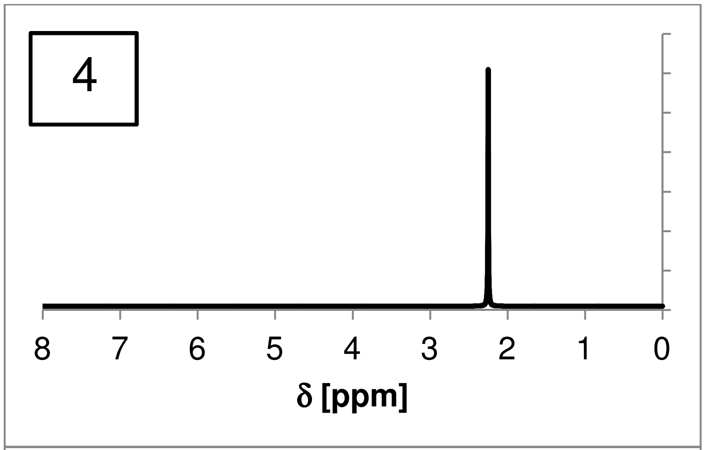
$$\text{(d)}\ \begin{cases} \Delta G_1^0 = -n_1F\varepsilon_1^0 = -2F\varepsilon_1^0 \\ \Delta G_2^0 = -n_2F\varepsilon_2^0 = -F\varepsilon_2^0 \\ \Delta G_3^0 = -n_3F\varepsilon_3^0 = -3F\varepsilon_3^0 \\ \Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0 \ \Rightarrow\ -3F\varepsilon_3^0 = -2F\varepsilon_1^0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

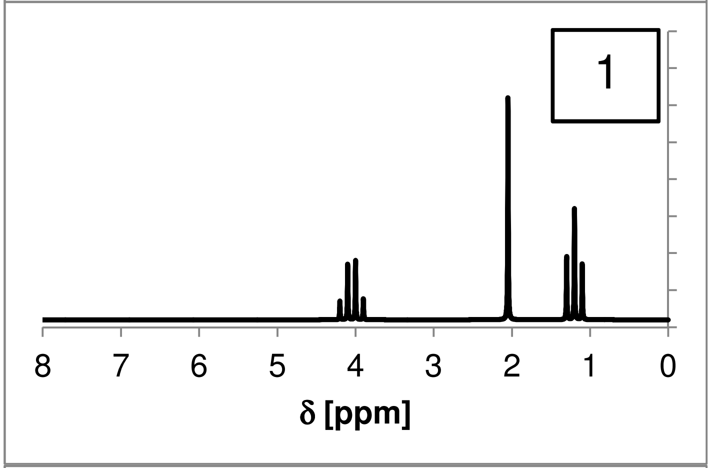
$$\text{OR:}\ \begin{cases} \text{Anode:} & \mathrm{Au}(s) \rightarrow \mathrm{Au^{3+}}(aq) + 3\mathrm{e^-} & -\varepsilon_3^0 & \Delta G_3^0 = 3F\varepsilon_3^0 \\ \text{Cathode:} & 3\mathrm{Au^+}(aq) + 3\mathrm{e^-} \rightarrow 3\mathrm{Au}(s) & +\varepsilon_2^0 & \Delta G_2^0 = -3F\varepsilon_2^0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

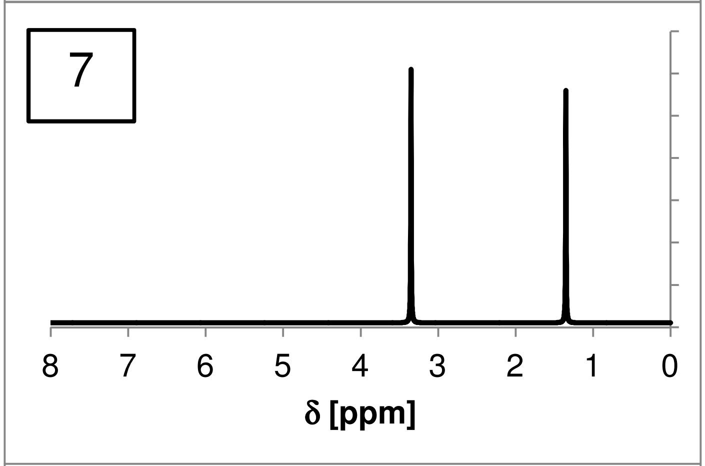
Part I: [6 marks] Assign the correct molecular formula (or structure) to each of the following ^{1}H NMR spectrum. Fill in the box using the appropriate number corresponding to a particular molecule, *e.g.*, $\boxed{8}$. There is only one correct formula (or structure) for each NMR spectrum. Note that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

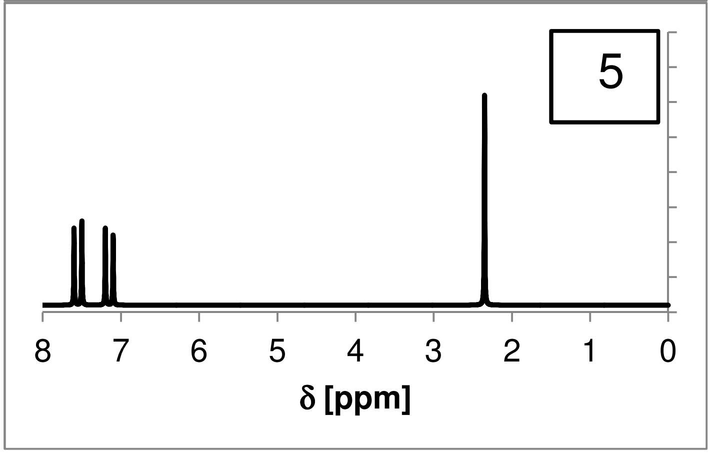
1)  $\mathrm{CH_3{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3}$
2) C_6H_6
3)  $\mathrm{CH_3{-}CH_2{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_3}$
4)  $\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3}$
5) $Br{-}C_6H_4{-}CH_3$
6) $(CH_3)_2CH{-}OH$
7) $(CH_3)_2C(OCH_3)_2$

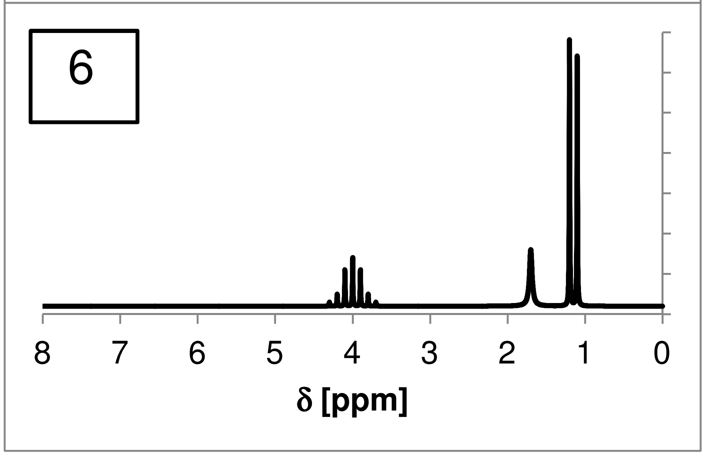




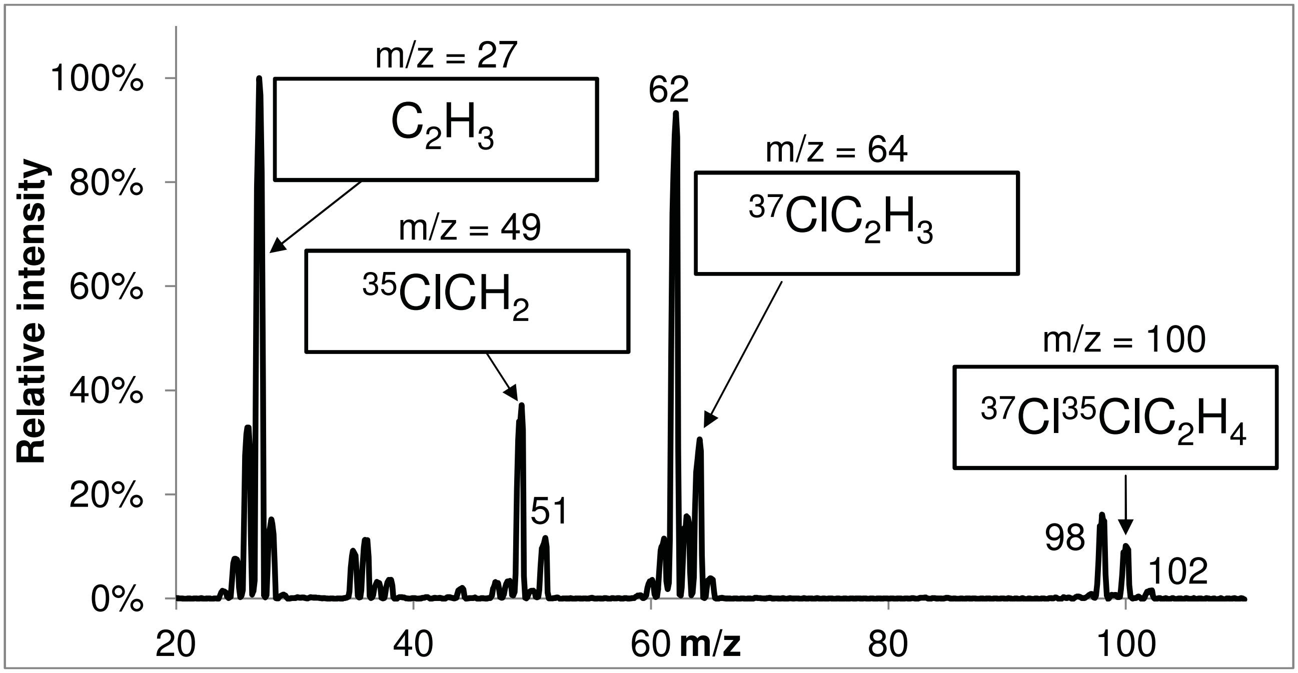








Part J: [5 marks] An undergraduate chemistry student collected a mass spectrum:

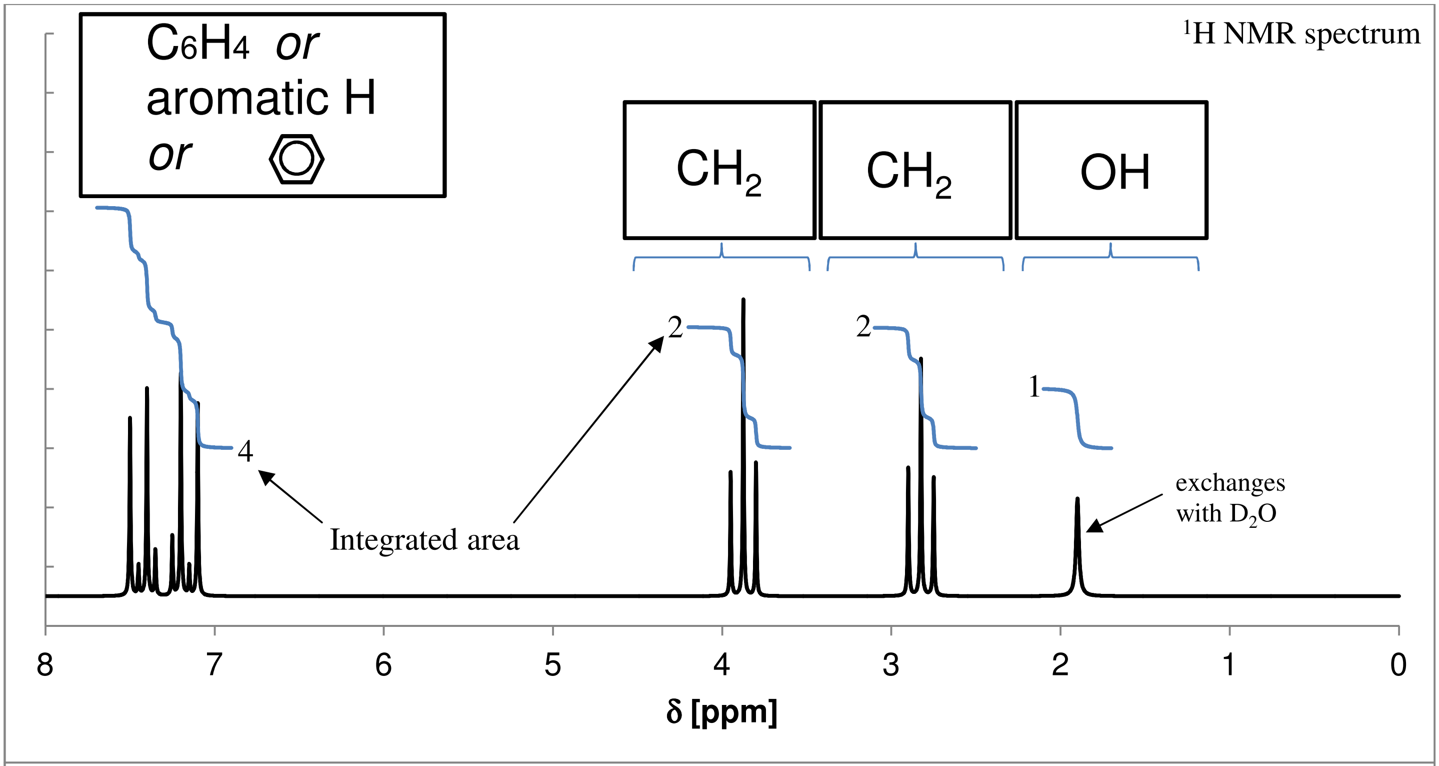


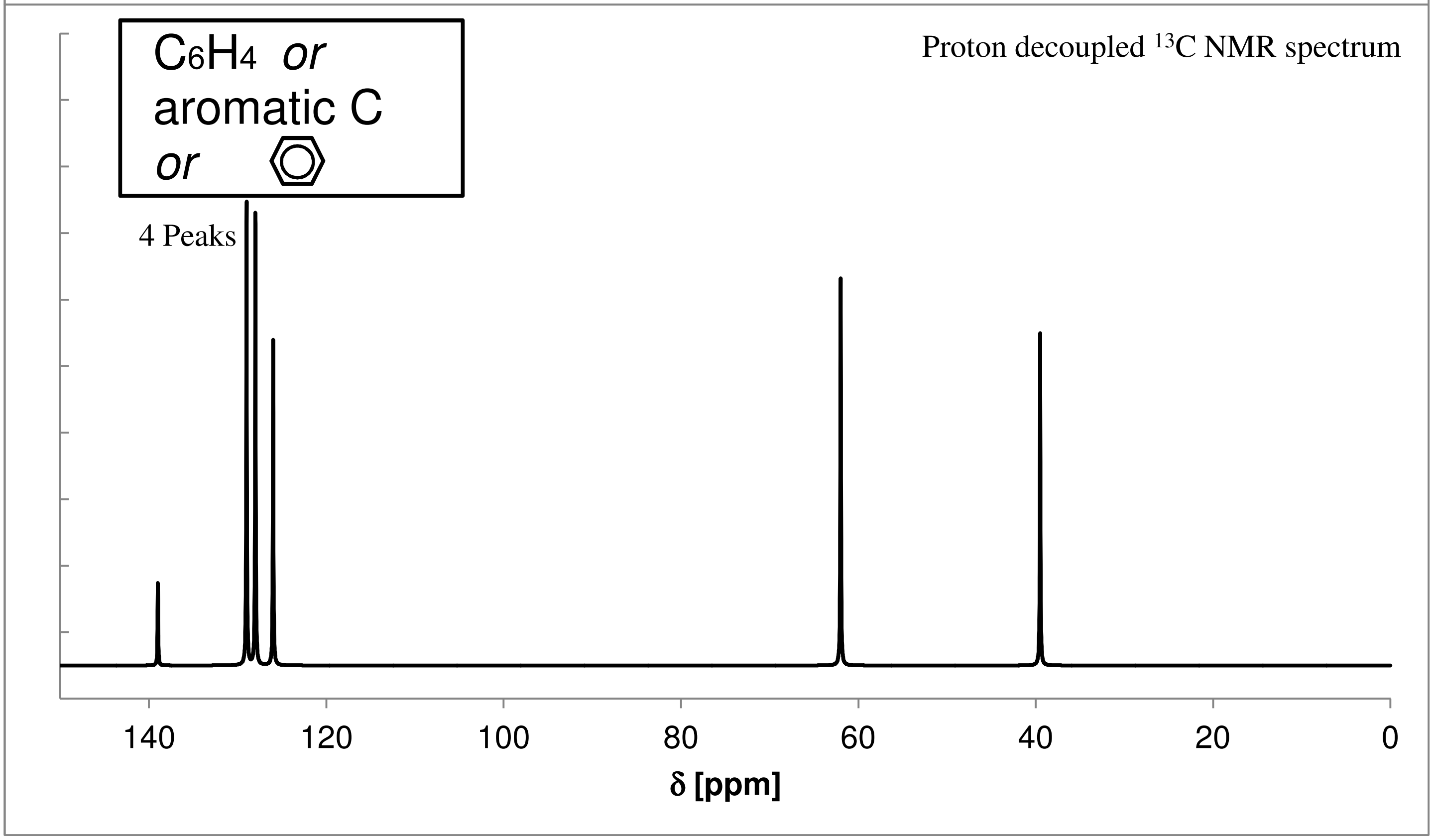
(a) [1 mark] Please identify which of the following molecule is responsible for the above mass spectrum? (circle one below)

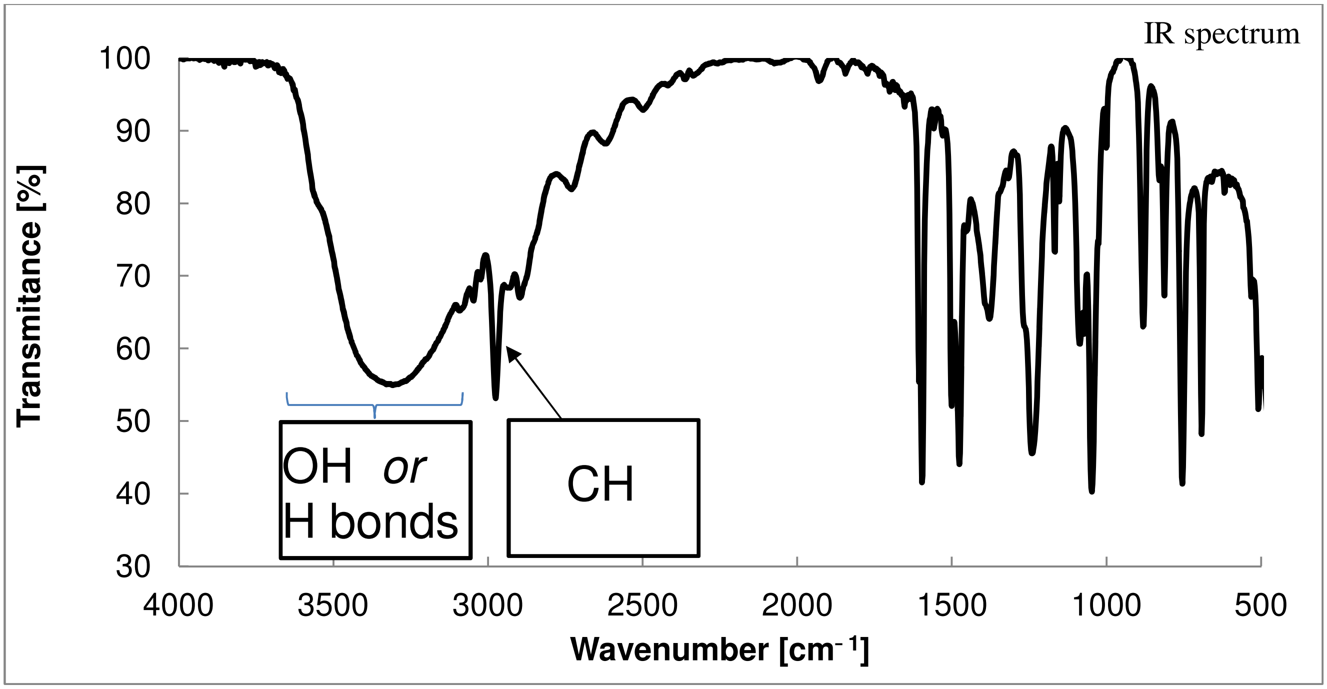
1) CH_2Cl_2
2) $CHCl_3$
3) C_2H_5Cl
[✓ 4) $C_2H_4Cl_2$]
5) CH_3Cl
6) $C_2H_3Cl_3$

(b) [4 marks] Then write the chemical formula **of the fragment** (of your chosen molecule) responsible for each labeled signal inside the boxes in the above mass spectrum. Be sure to clearly identify isotopes involved, for example: $\boxed{^{81}Br^{79}BrC_3H_6}$

Part K: [9 marks] The following spectra were collected for a compound of formula C_8H_9OCl. 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.







Draw the structure of the molecule in the box below: