THE UNIVERSITY OF BRITISH COLUMBIA
FINAL EXAMINATION, APRIL 2010

CHEMISTRY 205
(Physical Chemistry)

GIVEN NAME(S): _____ SURNAME: _____
(PRINT, CAPITALS)

STUDENT NUMBER: _____ SIGNATURE: _____

PLEASE CLEARLY IDENTIFY YOUR SECTION

Lecturer:	Dr. Straus / Burnell	sec 208	MWF 8AM	
	Dr. Straus / Burnell	sec 210	MWF 10AM	
	Dr. Straus / Burnell	sec 203	MWF 3PM	
	Dr. Li	sec 299	T TH 9:30AM	
	Dr. Signorell	sec 222	T TH 2PM	

THIS EXAMINATION CONSISTS OF 12 NUMBERED PAGES. PLEASE CHECK THAT YOU HAVE A COMPLETE EXAMINATION PAPER. PAGES 11 AND 12 ARE INFORMATION PAGES AND MAY BE SEPARATED FROM THE REST OF THE EXAM.

Attempt ALL EIGHT (8) questions. All work must be shown in this booklet. Time: 2.5 Hours

Question	Maximum	Mark
1	9	
2	10	
3	6	
4	10	
5	9	
6	8	
7	9	
8	9	
EXAM	70	

RULES GOVERNING EXAMINATIONS

1. EACH CANDIDATE SHOULD BE PREPARED TO PRODUCE, UPON REQUEST, HIS/HER LIBRARY/AMS CARD.
2. READ AND OBSERVE THE FOLLOWING RULES:
   No candidate shall be permitted to enter the examination room after the expiration of one-half hour, or to leave during the first half-hour of the examination.
   Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
   CAUTION - Candidates guilty of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action.

(a) Making use of any books, papers or memoranda, other than those authorized by the examiners.
(b) Speaking or communicating with other candidates.
(c) Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.

THE USE OF PROGRAMMABLE and GRAPHING CALCULATORS IS NOT PERMITTED
You must NOT remove this booklet from the examination room

1) [9 marks] In each part of this question give your answer in the box. There is only one correct answer for each part.

(a) The first law states:

A) entropy is zero for a perfect crystal of a pure substance at zero degrees absolute
B) the entropy of an isolated system increases for any spotaneous process
C) energy is conserved
D) heat flows spontaneously from a hot body to a cold body

(b) The half life of a chemical reaction does not depend on reactant concentration for a

A) zero-order reaction
B) first-order reaction
C) second-order reaction
D) none of the above because the half life always depends on the concentration

(c) UV (ultra-violet) spectroscopy results from transitions between

A) electronic energy levels
B) vibrational energy levels for a given electronic state
C) rotational energy levels for a given electronic state
D) nuclear-spin energy levels for a given electronic state

(d) $\Delta_r G^o$ is –3.4 kJ/mol at 25°C for the reaction

$$2\ HI\ (g) \leftrightarrow H_2(g) + I_2(s)$$

The standard Gibbs energy of formation $\Delta_f G^o$ of HI(g) at 25°C is:

A) −3.4 kJ/mol
B) +3.4 kJ/mol
C) −1.7 kJ/mol
D) +1.7 kJ/mol

(e) In the equation $\Delta G = \Delta G^o + RT \ln Q$

A) ΔG^o is the Gibbs energy of reaction at equilibrium
B) ΔG is the Gibbs energy of reaction
C) the reaction quotient Q always equals the ratio of activities at equilibrium
D) the equation $\Delta G^o = -RT \ln Q$ is always valid, even when $Q \neq K$

(f) The activation energy for a chemical reaction

A) is the energy barrier that describes the temperature dependence of the reaction rate
B) is ΔU for a chemical reaction
C) is ΔG for a chemical reaction
D) is 3/2 R per mol of an ideal monatomic gas

(g) You obtain an IR spectrum with a strong band at 1715 cm^{-1} and only weak bands in the 3000 cm^{-1} region. Which of the following molecules would give rise to such a spectrum?

A) $CH_3–CH_2–OH$
B) $CH_3–(C=O)–OH$
C) $CH_3–(C=O)–NH_2$
D) $CH_3–(C=O)–CH_2CH_3$
E) None of the above

(h) The elementary reaction

$$A + 2B \rightarrow C$$

A) is first-order in C and second-order in B
B) is an overall third-order reaction
C) is second order in both A and B
D) is second-order in B because A is a catalyst

(i) A 30 residue peptide extracted from amphibians has an extinction coefficient of 14105 $M^{-1}\ cm^{-1}$ at 280 nm in water. You prepare a solution and measure an absorbance of 0.45, using a cell of 1 cm path length. How concentrated is the solution you prepared?

A) 32 x 10^{-3} $mol.L^{-1}$
B) 32 x 10^{-6} $mol.L^{-1}$
C) 11 x 10^{-3} $mol.L^{-1}$
D) 11 x 10^{-6} $mol.L^{-1}$
E) None of the above

2) [10 marks]: A Chemistry 205 student proposes a process in which 2 mols of an ideal diatomic gas ($C_{v,m}$ = 5R/2), initially at 27°C and 1 atm pressure, do 4000 J of work on the surroundings while absorbing 3000 J of heat. During this process the volume of the gas doubles. The temperature of the surroundings is kept constant at 27°C. Calculate *w, q,* ΔU, the final temperature of the gas, ΔH, ΔS and ΔS_{total} for this process. **SHOW YOUR REASONING for all your answers**. Is this process spontaneous, reversible or impossible? – **explain your answer**.

	value	**units**
q =		
w =		
ΔU =		
T_{final}		
ΔH =		
ΔS =		
ΔS_{total} =		

Check the correct box – the process is: spontaneous ☐

reversible ☐

impossible ☐

why? ☐

3) [6 marks]

(a) [4 marks] The molar mass of an unknown substance is determined by osmotic pressure measurements performed at a temperature of $T = 298$ K. The measured osmotic pressure for an aqueous solution of this substance with a concentration of 10 g/L is 4.12 atm. Moreover, it is known that this substance does not dissociate in water. What is the molar mass of this substance?

ANSWER _____

(b) [2 marks] Determine the normal boiling point of a solution of 5 moles of this substance in 1 kg water. The ebullioscopic constant of water is $K_b = 0.51 \frac{\text{K} \cdot \text{kg}}{\text{mol}}$.

ANSWER _____

4) [10 marks] Rechargeable Li-ion batteries are used in all kinds of electronic equipment. Consider a simplified example:

Cell symbol: $Li(s) \mid Li^+(aq) \parallel Ni^{2+}(aq) \mid Ni(s)$

Stoichiometry of the cell reaction: $Ni^{2+} + 2Li = Ni + 2Li^+$ (*)

The standard electromotive force of the cell reaction is $E^0 = 2.82V$ at a temperature $T = 298K$. The standard electrode potential of the Ni half cell ($Ni^{2+} + 2e^- = Ni$) is −0.23 V.

(a) [2 marks] Is the cell reaction (*) spontaneous under standard conditions? **Give your reasoning.**

ANSWER _____

(b) [2 marks] Calculate the standard electrode potential of the Li half cell ($Li^+ + e^- = Li$).

ANSWER _____

(c) [2 marks] Calculate the standard Gibbs energy of reaction (*).

ANSWER _____

(d) [4 marks] The actual concentrations of both Ni^{2+} and Li^+ in the cell are 0.001 M. Calculate the reaction quotient Q and the electromotive force E for these concentrations.

ANSWERS Q = _____ E = _____

5) [9 marks]
The gas phase reaction $C_2H_6 + H_2 \rightarrow 2CH_4$ is believed to occur according to the following mechanism:

$1) C_2H_6 \rightarrow 2CH_3\cdot \quad (k_1)$
$2) 2CH_3\cdot \rightarrow C_2H_6 \quad (k_2)$
$3) CH_3\cdot + H_2 \rightarrow CH_4 + H\cdot \quad (k_3)$
$4) H\cdot + C_2H_6 \rightarrow CH_4 + CH_3\cdot \quad (k_4)$

Use the steady state approximation for both $CH_3\cdot$ and $H\cdot$ to show that the rate law for the above reaction follows:

$$\frac{d[CH_4]}{dt} = 2k_3\left(\frac{k_1}{k_2}\right)^{1/2}[C_2H_6]^{1/2}[H_2]$$

SS for $CH_3\cdot$

SS for $H\cdot$

$$\frac{d[CH_4]}{dt} =$$

6) [8 marks] The following first order gas phase reaction $A(g) \rightarrow 2B(g)$ was carried out at constant temperature in a reaction vessel of a constant volume. At the beginning of the reaction, only A at a pressure of 1 atm was present. After 10 minutes of reaction, the total pressure in the vessel reaches 1.5 atm. After a sufficiently long time, A was completely consumed. Assume that both A and B are ideal gases.

(a) Determine the rate constant k and half life $t_{½}$ of the reaction.

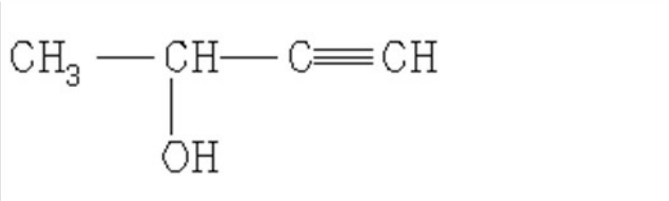
	value	units
k =	_____	_____
$t_{½}$ =	_____	_____

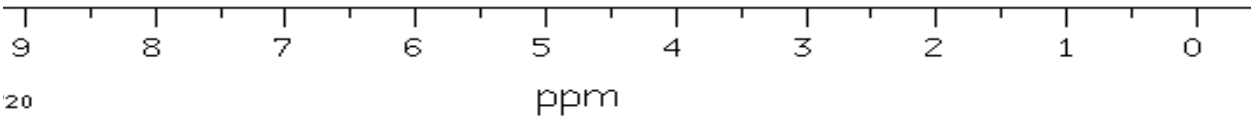
(b) If the activation energy of this reaction is E_a=229.3 kJ/mol, and the rate constant at 650 K is 2.14×10^{-4} s^{-1}, calculate the Arrhenius prefactor A.

	value	units
A =	_____	_____

7) [9 marks] A colleague hands you a NMR sample of C_4H_6O in water (see below for structure). Unfortunately your spectrometer is broken, so you have to sketch the expected ^1H NMR spectrum. Clearly indicate:
   (a) the approximate ^1H chemical shift for each type of H;
   (b) the splittings and the relative intensity ratios which arise from the J-coupling; and
   (c) the total integral for each group.

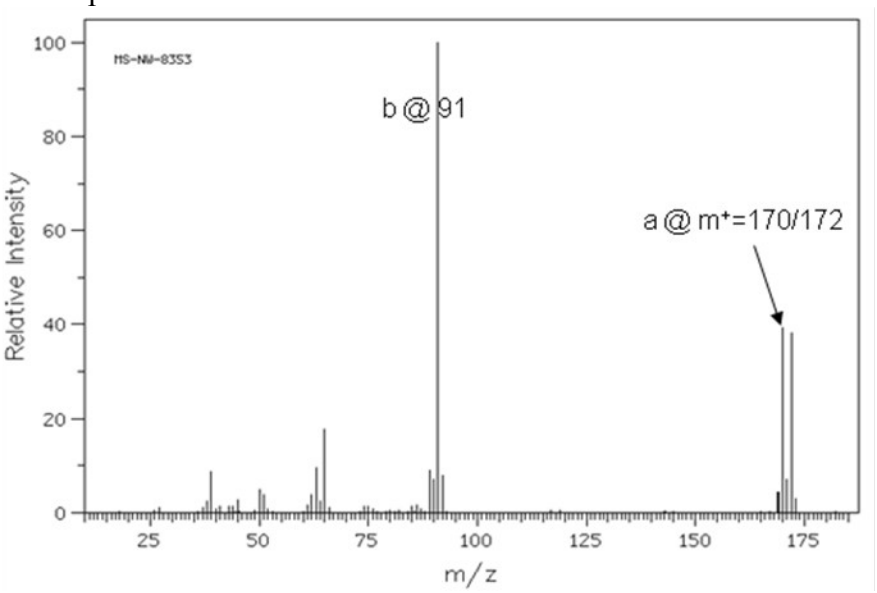
   Be sure to indicate if any ^1H's are exchanging with the solvent.





8) [10 marks] The following spectra were collected for a compound of formula C_7H_7Br. Identify the compound by drawing its structure in the box on the next page. Be sure to also explain which chemical moiety (e.g. $-CH_2CH_3$, $-CH_3$,...) gives rise to the peaks labelled a) through g). **<u>Be sure to show your reasoning</u>.**

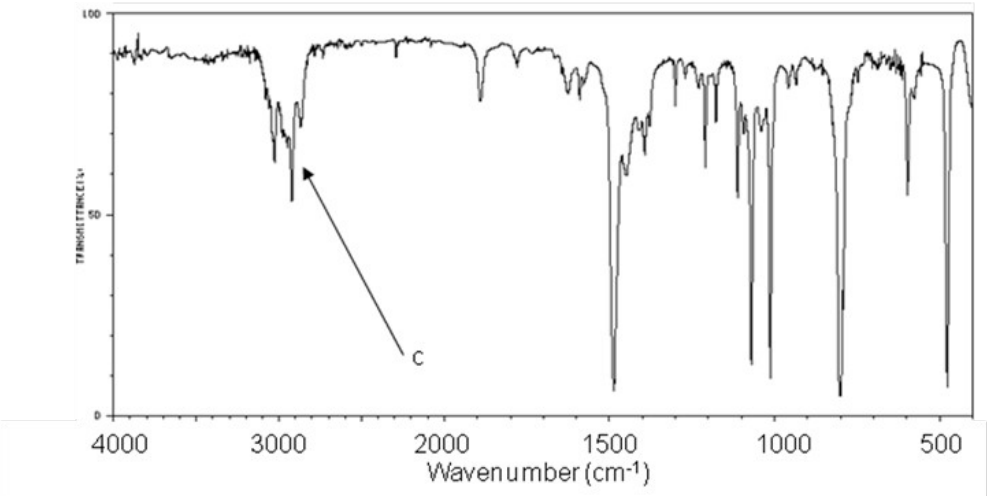
Mass spectrum:



a)_____

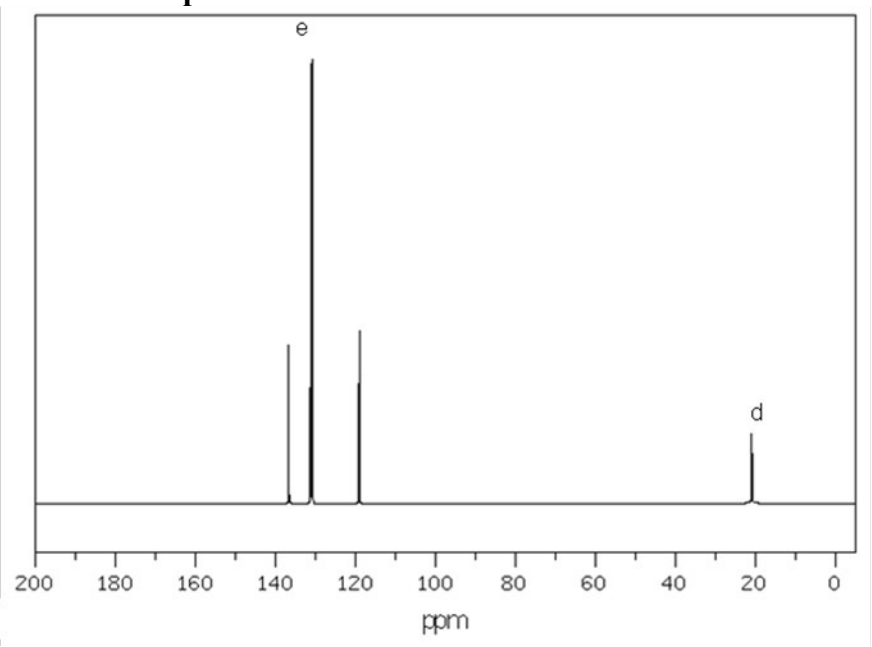
b)_____

IR spectrum:



c)_____

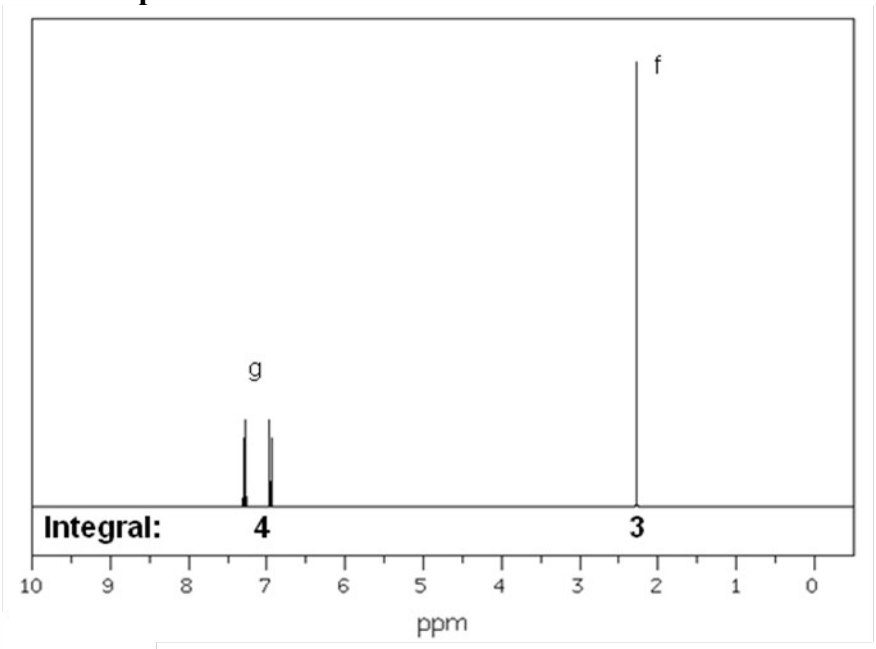
^{13}C NMR spectrum:



d) (quartet in H coupled ^{13}C NMR spectrum)_____

e) (4 lines)_____

^{1}H NMR spectrum:



f)_(singlet)_____

g)_(multiplet)_____

Answer: