

**UNIVERSITY OF TORONTO**  
**FACULTY OF ARTS AND SCIENCE**

**JUNE 2014 EXAMINATIONS**

**CHM220H1F EXAM**

Duration: 3 hours

Aids: Non-programmable calculator

Name: \_\_\_\_\_

Student Number: \_\_\_\_\_

Tutorial Section: \_\_\_\_\_

No.	Maximum	Mark
1.	20	
2.	11	
3.	13	
4.	12	
5.	14	
6.	14	
7.	16	
Total	100	

Write legibly! Use the back of a page if more space is required, and indicate clearly when you have done so.

**QUESTION 1 (20 pts)**

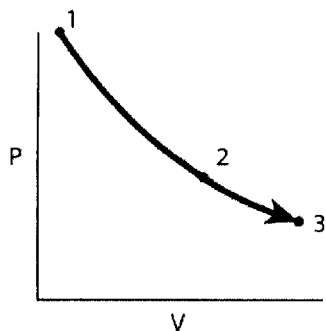
The graphs below illustrate an isothermal reversible expansion (i) or compression (ii) that goes through three points: 1, 2 and 3.

The temperature is kept at **300 K**, and the respective pressures at points 1, 2, and 3 are:

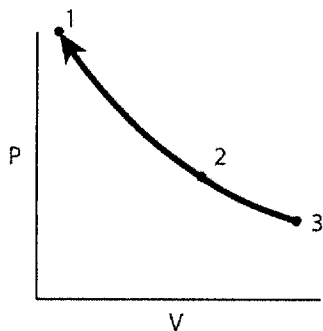
**$P_1 = 4 \text{ atm}$ ,  $P_2 = 2 \text{ atm}$ , and  $P_3 = 1 \text{ atm}$**

(a) [2 pts] On the graphs below, sketch the work done in a two-step series of irreversible **expansion (i)** (1-2-3) and **compression (ii)** (3-2-1) processes at constant pressure.

i)



ii)



(b) [4 pts] Calculate the values of  **$w$ ,  $q$ ,  $\Delta H$  and  $\Delta U$**  for a **reversible isothermal expansion** of 1 mole of monatomic ideal gas. The gas is initially at point 1, where  $P_1 = 4 \text{ atm}$ , and expands to point 3, where  $P_3 = 1 \text{ atm}$ .

(c) [2 pts] Calculate the work done for an **irreversible isothermal expansion** of 1 mole of monatomic ideal gas in the two-step process (1  $\rightarrow$  2  $\rightarrow$  3) described in part (a).

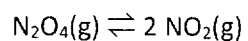
(d) [5 pts] In another experiment, one mole of an ideal monatomic gas is initially at 300 K and 4 atm and expands to a final pressure of 1 atm. Calculate the values of  $w$ ,  $q$ ,  $\Delta H$  and  $\Delta U$  if the expansion occurred via an **adiabatic and reversible** path.

(e) [2 pts] Use a PV-diagram to illustrate the difference in values for work that you obtained in part (d) (reversible adiabatic expansion) and (b) (reversible isothermal expansion). Note that both processes had the same starting point, and the gases expanded to the same final pressure.

(f) [5 pts] In the next experiment, one mole of an ideal monatomic gas is initially at 300 K and 4 atm and expands against a constant pressure to a final pressure of 1 atm. Calculate the values of  $w$ ,  $q$ ,  $\Delta H$  and  $\Delta U$  if the expansion occurred via an **adiabatic and irreversible** path.

**QUESTION 2 [11 pts]**

(a) [7 pts] Dinitrogen tetroxide is 18.46 percent dissociated at 25°C and 1.00 bar in the equilibrium



Calculate/determine the following:

(i) K at 25°C

(ii)  $\Delta_r G^\circ$

(iii)  $\Delta_r G$

(iv) K at 100°C given that  $\Delta_r H^\circ = 57.2 \text{ kJ mol}^{-1}$  over the temperature range.

(b) [4 pts] The standard Gibbs energy of formation of  $\text{NH}_3(\text{g})$  is  $-16.5 \text{ kJ mol}^{-1}$  at 298 K.

(i) What is the reaction Gibbs energy when the partial pressure of the  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  (treated as ideal gases) are 3.0 bar, 1.0 bar, and 4.0 bar, respectively?

(ii) What is the spontaneous direction of the reaction in this case?

**QUESTION 3 (13 pts)**

In the table below fill in the following fields:

- (a) [3 pts] Write the differential rate expression ( $d[A]/dt$ ) for all three of the cases.  
 (b) [3 pts] Sketch (no exact values needed, just trends) the change in concentrations of reactants and products over time for all the three cases, keeping in mind the relative rate constants that have been provided.

	I Reversible reaction $A \xrightleftharpoons[k_{-1}]{k_1} B$	II Sequential first-order reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$	III Parallel reaction $A \xrightarrow{k_B} B$ $A \xrightarrow{k_C} C$
a)			
b)	$k_1 = 2k_{-1}$ $\frac{[X]}{[A_0]}$ time	$k_1 = 3k_2 = 0.3s^{-1}$ $\frac{[X]}{[A_0]}$ time	$3k_B = k_C$ $\frac{[X]}{[A_0]}$ time

(c) [1 pts] For the reversible reaction (Column I), determine the equilibrium constant  $K$ .

(d) [4 pts] For the sequential first-order reaction (Column II), determine the time at which  $[B]$  is at a maximum.

Given:  $[B] = \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) [A]_0$

(e) [2 pts] In the case of the parallel reaction (Column III), what is the yield for the formation of product C?

#### QUESTION 4 (12 pts)

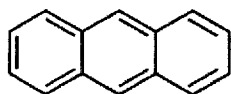
Briefly answer the following questions.

(a) [3 pts] Determine the most probable radius at which an electron will be found when it occupies the 1s orbital, if the 1s radial distribution function is (show your work):

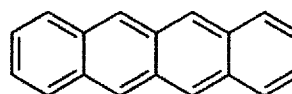
(b) [3 pts] Sketch the  $4d_{xy}$  orbital showing the axes, the relative phases, and being careful to respect the three-dimensional nature of the orbitals. Determine the number of radial and angular nodes.

(d) [3 pts] Use the Frost-Musulin diagram (polygon in a circle) determine the energy levels of each MO in terms of  $\alpha$  and  $\beta$  for cyclobutadiene ( $C_4H_4$ ). Show the electrons in the corresponding orbitals.

(e) [3 pts] Explain why anthracene is colourless, but tetracene is light orange. Also, what colour does anthracene emit?



Anthracene



Tetracene

**QUESTION 5 (14 pts)**

(a) [4 pts] Normalize the total energy eigenfunction for the three-dimensional box and show your work.

**Given:**  $\psi_{n_x, n_y, n_z} = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)$        $\int A \sin^2(bx) dx = A \left[ \frac{x}{2} - \frac{\sin 2bx}{4b} + c \right]$

$n_x = 1, 2, 3, \dots$      $n_y = 1, 2, 3, \dots$      $n_z = 1, 2, 3, \dots$

(b) [5 pts] Determine the wavefunctions and energy for the **second excited level** of a particle in a **cubic box** of edge  $a$ . What is the degeneracy of this level?

**Given:**  $E = \frac{h^2}{8m} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$

Combinations of  $n_x, n_y, n_z = (122) (212) (221)$  – three fold degenerate

(c) [3 pts] If the box is such that  $a < b < c$ , what would happen to the degeneracy of the energy level determined in (a)? Comment on the relative values of the resulting energy levels.

(d) [2 pts] If the particle is confined to a 3D box that has sides  $a, b=2a, c=3a$ . Give the quantum numbers that correspond to the lowest four quantum states of this box. (Hint: it might be easier to show energies in the units of  $h^2/288ma^2$ )

$n_x$	$n_y$	$n_z$	Energy ( $h^2/288ma^2$ )

**QUESTION 6 (14 pts)**

- (a) [3 pts] The typical energy differences for transitions in the electronic, microwave, and IR spectroscopies are given in the table below in no particular order. Assign the values of the energy differences to the three kinds of transitions.

Energy Difference	Transition
$5 \times 10^{-22} \text{ J}$	
$0.5 \times 10^{-19} \text{ J}$	
$1 \times 10^{-18} \text{ J}$	

- (b) [7 pts] Calculate the ratio of the number of molecules in two adjacent energy levels (the ground state and the first excited level) at 300 K in each case.

Electronic:

Microwave:

IR:

- (c) [1 pts] What happens to the population ratio calculated in (b) when the temperature is increased?

Increases

Decreases

Stays the Same

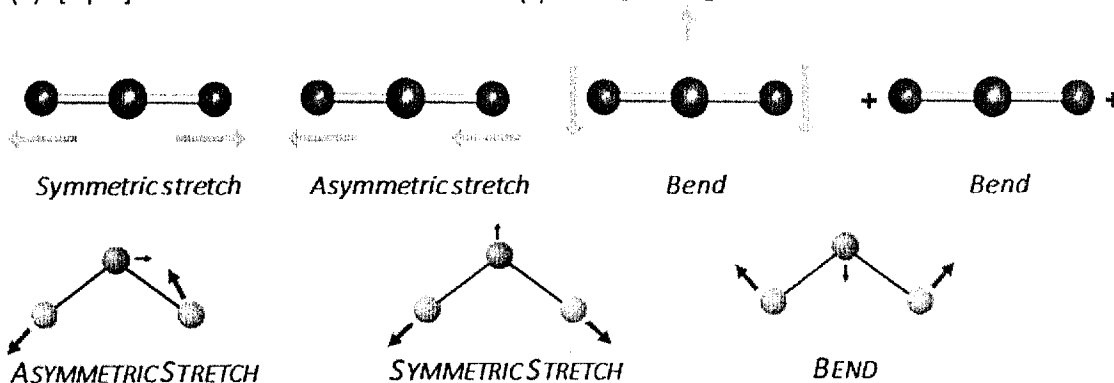
- (d) [1 pts] What happens to the population ratio calculated if we compare the ground state and the second excited level at 300 K?

Increases

Decreases

Stays the Same

- (e) [2 pts] Below circle which of the mode(s) of CO<sub>2</sub> and H<sub>2</sub>O are IR active.



**QUESTION 7 (16 pts)**

(a) [6 pts] Sketch a Jablonski diagram illustrating energy transfer for a donor-acceptor pair. Make sure to include  $S_0$  and  $S_1$  states of both chromophores and the  $T_1$  state of the donor. Label the following processes on the diagram:

$$\text{For the Donor: } k_{\text{rad}}(S_1 \rightarrow S_0) = 7.0 \times 10^9 \text{ s}^{-1}; \quad k_{\text{IC}}(S_1 \rightarrow S_0) = 4.0 \times 10^{10} \text{ s}^{-1}; \quad k_{\text{ISC}}(S_1 \rightarrow T_1) = 1.5 \times 10^8 \text{ s}^{-1}$$
$$k_{\text{RET}} = 2.0 \times 10^{11} \text{ s}^{-1}$$

(b) [4 pts] Calculate the fluorescence life time of the donor and the efficiency of the energy transfer.

(c) [2 pts] Circle the correct answer (possible answers are underlined).

i) Fluorescence of the donor is red-shifted / blue shifted compared to that of the acceptor.

ii) Increase in the distance between the donor and the acceptor will result in the decrease / increase of the rate of resonance energy transfer.

(d) [4 pts] An aqueous solution of the donor (**D**) and the acceptor (**A**) has an absorbance of 0.326 at 320 nm and 0.532 at 270 nm. The molar absorptivities of **D** and **A** are:

$$\text{D: } \epsilon_{320} = 2.72 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \quad \text{A: } \epsilon_{320} = 3.46 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$
$$\epsilon_{270} = 5.35 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \quad \epsilon_{270} = 4.12 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

If the path length of the cell is 1.00 cm, calculate the concentration of A and B in mol L<sup>-1</sup>.

## CONSTANTS AND CONVERSION FACTORS

### Physical and Chemical Constants

Atomic mass unit	$1 \text{ a.m.u.} = 1.6605402 \times 10^{-27} \text{ kg}$
Mass of an electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Mass of a neutron	$m_n = 1.674 \times 10^{-27} \text{ kg}$
Mass of a proton	$m_p = 1.672 \times 10^{-27} \text{ kg}$
Avogadro's number	$N_A = 6.0221367 \times 10^{23} \text{ mole}^{-1}$
Boltzmann's constant	$k = 1.380658 \times 10^{-23} \text{ J K}^{-1}$
Faraday's constant	$F = 9.6485309 \times 10^4 \text{ C mole}^{-1}$
Fundamental unit charge	$e = 1.60217733 \times 10^{-19} \text{ C}$
Gas constant	$R = 8.314510 \text{ J mole}^{-1} \text{ K}^{-1}$ $= 0.08315 \text{ bar dm}^3 \text{ mole}^{-1} \text{ K}^{-1}$ $= 0.082058 \text{ L atm mole}^{-1} \text{ K}^{-1}$
Heat capacity of water	$C = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$ $= 75.4 \text{ J mole}^{-1} \text{ K}^{-1}$
Planck's constant	$h = 6.6260755 \times 10^{-34} \text{ J s}$
Rydberg's constant	$R_H = 2.1798 \times 10^{-18} \text{ J}$ $= 1.097 \times 10^{-2} \text{ nm}^{-1}$
Speed of light	$c = 2.99792458 \times 10^8 \text{ m s}^{-1}$
Zero point	$0^\circ\text{C} = 273.15 \text{ K}$
$K_w$ of $\text{H}_2\text{O}$ at $25^\circ\text{C}$	$K_w = 1.00 \times 10^{-14}$
Pi	$\pi = 3.1415927$

### CONVERSION FACTORS

1 atmosphere (atm)	$= 1.01325 \times 10^5 \text{ Pa (N m}^{-2}\text{)} = 760.0 \text{ mm Hg (torr)} = 1.01325 \text{ bar}$
1 calorie (cal)	$= 4.184 \text{ joules (J)}$
1 debye (D)	$= 3.335617 \times 10^{-30} \text{ C m}$
1 eV/particle	$= 96.485 \text{ kJ mole}^{-1} = 23.061 \text{ kcal mole}^{-1}$
1 eV	$= 1.602 \times 10^{-19} \text{ J} = 8067 \text{ cm}^{-1}$
1 kcal mole <sup>-1</sup>	$= 4.184 \text{ kJ mole}^{-1} = 349.73 \text{ cm}^{-1}$
1 kJ mole <sup>-1</sup>	$= 0.23901 \text{ kcal mole}^{-1} = 83.591 \text{ cm}^{-1}$
1 L atm	$= 101.325 \text{ J} = 24.217 \text{ cal}$
ln x	$= 2.3026 \log x$

EQUATION SHEET

$PV = nRT$ $P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$	$\Delta U = q + w$ $dU = nC_{v,m}dT$ $H = U + PV$ $dH = nC_{p,m}dT$
$dw = -P_{ext}dV$ $W_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$	$\Delta H^{\circ}_{rxn} = \sum u_i \Delta H^{\circ}_{f,i} + \Delta C_p (T - 25^{\circ}C)$ $\Delta C_p = \sum u_i C_{p,i}$ For ideal gases, $C_{p,m} = C_{v,m} + R$
$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$ $T_1 V_1^{(\gamma-1)} = T_2 V_2^{(\gamma-1)}$ $\left(\frac{\bar{C}_p}{\bar{C}_v}\right) = \gamma$ $T_1 P_1^{((1-\gamma)/\gamma)} = T_2 P_2^{((1-\gamma)/\gamma)}$	Efficiency = $ w /q_{in}$ $\epsilon = 1 - T_C/T_H$
$dS \equiv \frac{dQ_{reversible}}{T}$ $\Delta S^{\circ}(T_2) = \Delta S^{\circ}(T_1) + \int_{T_1}^{T_2} \Delta C_p \frac{dT}{T}$ $\Delta S^{\circ} = \sum coeff_p S^{\circ}(pdts) - \sum coeff_r S^{\circ}(rcts)$ $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$ $S = k \ln W$	$\Delta S = nR \ln \frac{V_f}{V_i}$ $\Delta S = nC_v \ln \frac{T_f}{T_i}$ $\Delta S = nC_p \ln \frac{T_f}{T_i}$
$\Delta P_1 = P_1^* x_2$ $P_2 = K' m$ $\pi = MRT$ $S_{gas} = K_H P_{gas}$	$P_1 = a_1 P_1^*$ $\Delta P_1 = a_2 P_1^*$ $a_1 = \gamma x_1$ $a_2 = \gamma x_2$
$\ln\left(\frac{K(T_1)}{K(T_2)}\right) = -\frac{\Delta H^{\circ}_{reaction}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ $\frac{dP}{dT} = \frac{\Delta \bar{H}}{T \Delta \bar{V}}$ $\frac{dP}{dT} = \frac{P \Delta_{vap} \bar{H}}{RT^2}$	$E = h\nu$ $\lambda = c/\nu$ $\lambda = h/mv$ $E_{photon} = h\nu_0 + E_k$ $E_n = -R_H Z^2/n^2$
First order reaction: $\ln\{[A]_0/[A]\} = kt$ Second order reaction: $1/[A] - 1/[A]_0 = kt$ Zero order reaction: $[A] = -kt + [A]_0$ Arrhenius equation: $k = Ae^{-E_a/RT}$	Particle in a 1D box $E_n = \frac{n^2 h^2}{8mL^2}$ $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$
$-\log \frac{I}{I_0} = -\log T = A$ $A = \epsilon bc$	$E_{rot} = \frac{J(J+1)h^2}{8\pi^2 I}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$ $I = \mu r^2$ $E_{vib} = \left(\nu + \frac{1}{2}\right) h\nu$ $\frac{n_i}{n_j} = \frac{g_i}{g_j} e^{-(E_i - E_j)/k_B T}$

# PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

PERIOD	GROUP 1 IA		GROUP NUMBERS IUPAC RECOMMENDATION (1985)										GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)						GROUP 18 VIIIA	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	1.0079 <b>H</b> HYDROGEN																	4.0026 <b>He</b> HELIUM		
2	6.941 <b>Li</b> LITHIUM	9.0122 <b>Be</b> BERYLLIUM											10.811 <b>B</b> BORON	12.011 <b>C</b> CARBON	14.007 <b>N</b> NITROGEN	15.999 <b>O</b> OXYGEN	18.998 <b>F</b> FLUORINE	20.180 <b>Ne</b> NEON		
3	22.990 <b>Na</b> SODIUM	24.305 <b>Mg</b> MAGNESIUM											26.982 <b>Al</b> ALUMINIUM	28.086 <b>Si</b> SILICON	30.974 <b>P</b> PHOSPHORUS	32.065 <b>S</b> SULPHUR	35.453 <b>Cl</b> CHLORINE	39.948 <b>Ar</b> ARGON		
4	39.098 <b>K</b> POTASSIUM	40.078 <b>Ca</b> CALCIUM											69.723 <b>Ga</b> GALLIUM	72.64 <b>Ge</b> GERMANIUM	74.922 <b>As</b> ARSENIC	78.96 <b>Se</b> SELENIUM	79.904 <b>Br</b> BROMINE	83.80 <b>Kr</b> KRYPTON		
5	85.468 <b>Rb</b> RUBIDIUM	87.62 <b>Sr</b> STRONTIUM											114.82 <b>In</b> INDIUM	118.71 <b>Sn</b> TIN	121.76 <b>Sb</b> ANTIMONY	127.60 <b>Te</b> TELLURIUM	126.90 <b>I</b> IODINE	131.29 <b>Xe</b> XENON		
6	132.91 <b>Cs</b> CAESIUM	137.33 <b>Ba</b> BARIUM	57-71 <b>La-Lu</b> Lanthanide										204.38 <b>Tl</b> THALLIUM	207.2 <b>Pb</b> LEAD	208.98 <b>Bi</b> BISMUTH	(209) <b>Po</b> POLONIUM	(210) <b>At</b> ASTATINE	(222) <b>Rn</b> RADON		
7	(223) <b>Fr</b> FRANCIUM	(226) <b>Ra</b> RADIUM	89-103 <b>Ac-Lr</b> Actinide																289 <b>Uuq</b> UNUNQUADIUM	

## LANTHANIDE

57 138.91 <b>La</b> LANTHANUM	58 140.12 <b>Ce</b> CERIUM	59 140.91 <b>Pr</b> PRASEODYMIUM	60 144.24 <b>Nd</b> NEODYMIUM	61 (145) <b>Pm</b> PROMETHIUM	62 150.36 <b>Sm</b> SAMARIUM	63 151.96 <b>Eu</b> EUROPIUM	64 157.25 <b>Gd</b> GADOLINIUM	65 158.93 <b>Tb</b> TERBIUM	66 162.50 <b>Dy</b> DYSPROSIUM	67 164.93 <b>Ho</b> HOLMIUM	68 167.26 <b>Er</b> ERBIUM	69 168.93 <b>Tm</b> THULIUM	70 173.04 <b>Yb</b> YTTERIUM	71 174.97 <b>Lu</b> LUTETIUM
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## ACTINIDE

89 (227) <b>Ac</b> ACTINIUM	90 232.04 <b>Th</b> THORIUM	91 231.04 <b>Pa</b> PROTACTINIUM	92 238.03 <b>U</b> URANIUM	93 (237) <b>Np</b> NEPTUNIUM	94 (244) <b>Pu</b> PLUTONIUM	95 (243) <b>Am</b> AMERICIUM	96 (247) <b>Cm</b> CURIUM	97 (247) <b>Bk</b> BERKELIUM	98 (251) <b>Cf</b> CALIFORNIUM	99 (252) <b>Es</b> EINSTEINIUM	100 (257) <b>Fm</b> FERMIUM	101 (258) <b>Md</b> MENDELEVIUM	102 (259) <b>No</b> NOBELIUM	103 (262) <b>Lr</b> LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 867-883 (2001)  
Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netinf.com)

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