UNIVERSITY OF TORONTO
FACULTY OF ARTS AND SCIENCE

JUNE 2015 EXAMINATIONS

CHM220 EXAM

Duration: 3 hours

Exam Aid Allowed: Non-Programmable Calculator

Name:______________________ Student Number:______________________

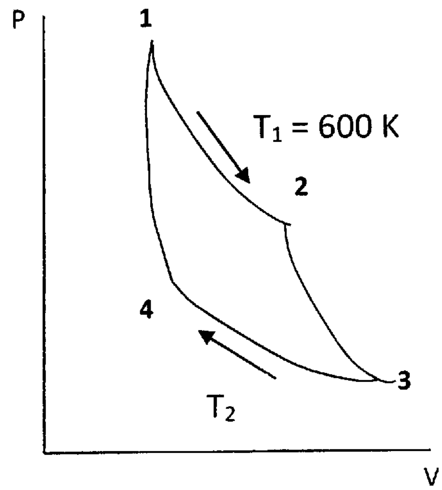
Tutorial Section:____________

No.	Maximum	Mark
1.	16	
2.	10	
3.	10	
4.	20	
5.	13	
6.	17	
7.	14	
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 [16 pts]

Consider the Carnot cycle shown below for 0.700 moles of an ideal ***monatomic*** gas for which you are given: $T_1 = 600$ K, $V_2 = 2V_1$ and $3V_3 = 4V_2$



(a) [3 pts] Calculate $w_{1\rightarrow2}$, $\Delta U_{1\rightarrow2}$, $q_{1\rightarrow2}$

(b) [2 pts] Find T_2.

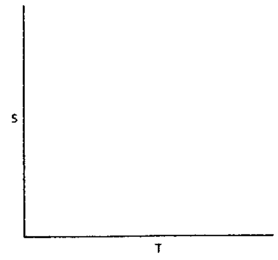
(c) [1 pts] What is the efficiency of a Carnot engine operating on this cycle?

(d) [2 pts] What is the total work around the cycle?

(e) [2 pts] How much heat is evolved at T_2?

(f) [2 pts] Evaluate $\Delta S_{3\rightarrow4}$.

(g) [2 marks] The above diagram shows a Carnot cycle in the form of a pressure-volume diagram. Sketch the corresponding entropy-temperature diagram, labeling the individual steps A→ B (isothermal), B→ C (adiabatic), C→ D (isothermal), and D → A (adiabatic).



(h) [2 pts] What is $\Delta S_{universe}$ for the whole cycle? Show your calculation or explain your result.

QUESTION 2 [10 pts]

Consider the reaction $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ for which K_P is found to have the following values:

T	600°C	1000°C
K_P	0.900	0.396

(a) [8 pts] Calculate $\Delta_r G°$, $\Delta_r S°$, and $\Delta_r H°$ for this reaction at 600°C. Assume that $\Delta_r H°$ is independent of temperature.

(b) [2 pts] Calculate the mole fraction of $CO_2(g)$ present in the gas phase at 600°C.

QUESTION 3 (10 pts)

(a) [3 pts] Sketch a Jablonski diagram and make sure to include the S_0, S_1, and T_1 states of the chromophore. Label the following processes on the diagram:

$k_{rad}(S_1 \rightarrow S_0)$ $k_{IC}(S_1 \rightarrow S_0)$ $k_{ISC}(S_1 \rightarrow T_1)$

(b) [3 pts] Assume that initially the chromophore is in the first excited state and $[S_0] = [T_1] = 0$. Using the rate constants provided in (a), write down expressions for $\frac{d[S_1]}{dt}$, $\frac{d[S_0]}{dt}$ and $\frac{d[T_1]}{dt}$.

Hint: This is a case of parallel reactions.

(c) [4 pts] Using rate constants provided in (a), write down expressions for:

i) The fluorescence lifetime of the chromophore

ii) The yield of S_0

iii) The yield of T_1

iv) $\frac{[S_0]}{[T_1]}$

QUESTION 4 (20 pts)

Briefly answer the following questions.

(a) [4 pts] Which of the following wave functions are eigenfunctions of the operator d^2/dx^2? If they are eigenfunctions, what is the eigenvalue? Show your work.

i) e^{-ikx}

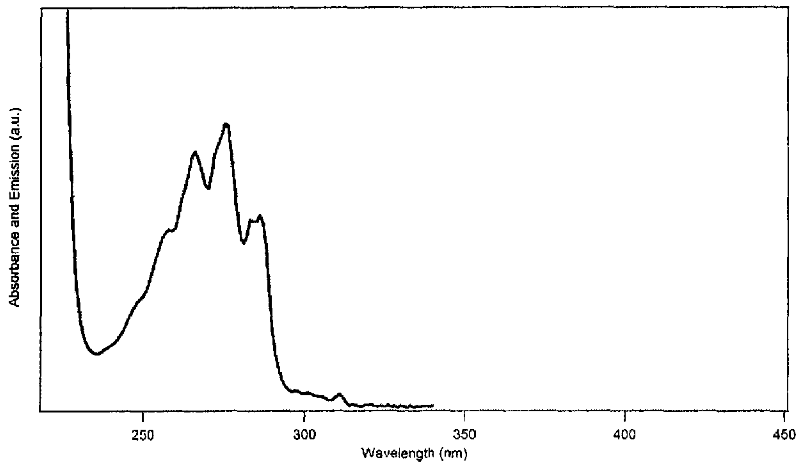
ii) $e^{-\alpha x^2}$

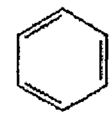
(b) [7 pts] Sketch the $4d_{z^2}$ orbital showing the axes, the relative phases, and being careful to respect the three-dimensional nature of the orbitals. Determine the number of radial and angular nodes. Also sketch the radial probability density function and the corresponding wavefunction.

(c) [3 pts] Locate the radial nodes in the 4p orbital of an H atom. The radial wavefunction $R_{4,1}$ is proportional to:

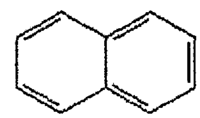
$(20-10\rho + \rho^2)\rho$ where $\rho = \frac{2Zr}{na_0}$ $a_0 = 0.529Å$

(d) [3 pts] The spectrum below shows the absorption of naphthalene. On the same graph, use a **solid line** to sketch the absorption of benzene and a **dotted line** for the emission of naphthalene. Indicate the Stokes' shift for naphthalene





benzene



naphthalene

(e) [3 pts] Describe how resonance energy transfer can be used to determine the separation between two molecules (Spectroscopic ruler).

QUESTION 5 (13 pts)

(a) [10 pts] Prepare a qualitative **molecular orbital energy level diagram** for BrCl. Use sketches to show clearly how the atomic orbitals interact to form MOs and clearly indicating the relative amount of electron density on each atom. Include labels for each molecular orbital giving the appropriate symmetry.

(b) [3 pts] What is the bond order? Would you expect BrCl to have a shorter or longer bond length than $BrCl^-$?

QUESTION 6 (17 pts)

(a) [7.5 pts] If a particle is confined to a 3D cubic box with edge length L=a=b=c , fill in the table below by indicating the energy the first five energy levels. Also, provide (n_x, n_y, n_z) for all the states as well as the degeneracy for each of the first five levels.

Given:

$$\psi_{n_x,n_y,n_z} = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right)$$

$$\int A\sin^2(bx)dx = A\left[\frac{x}{2} - \frac{\sin 2bx}{4b} + c\right]$$

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

n_x = 1, 2, 3, ... n_y = 1, 2, 3, ... n_z = 1, 2, 3, ...

Energy Level	Energy	(n_x, n_y, n_z)	Degeneracy
5			
4			
3			
2			
1			

(b) [4 pts] Consider an electron in a cubic box of 1 nm on a side. Calculate the ratio of the probabilities (N_2/N_1) of finding the electron in the first two energy levels at

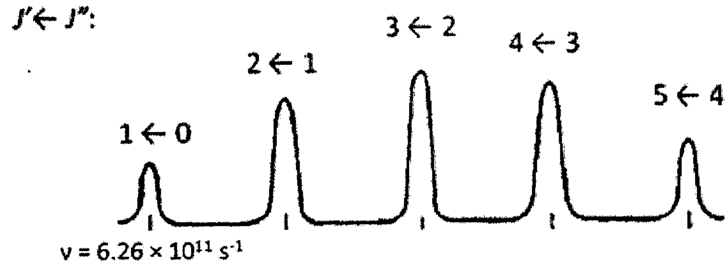
i) 10 K ii) 10'000 K

(c) [4.5 pts] With what probability will the particle described by the wavefunction in (a) be found in the volume $0 < x, y, z < L/4$ in the ground state?

(d) [1 pts] What would be the probability of finding the particle in the region described in (d) if the box was classical?

QUESTION 7 (14 pts)

(a) [6 pts] Below is a rotational spectrum of $H^{35}Cl$. Use the frequency for the J=0 to J=1 transition to determine the equilibrium internuclear distance R_e.



(b) [1 pts] Calculate the moment of inertia for $H^{35}Cl$.

(c) [4 pts] Calculate the difference in rotational energy between J = 1 and J = 2 levels and determine the wavelength of radiation that will be absorbed in promoting the molecule from J = 1 to J = 2. Show your work.

(d) [1 pts] What is the degeneracy of the rotational level with J = 5?

(e) [1 pts] What is the number of vibrational modes for HCl?

(f) [1 pts] Which of the following has the highest fundamental frequency of vibration? Circle the correct answer.

$H^{35}Cl$ $D^{35}Cl$

Physical and Chemical Constants

Atomic mass unit	1 a.m.u. = $1.6605402 \times 10^{-27}$ kg
Mass of an electron	$m_e = 9.109 \times 10^{-31}$ kg
Mass of a neutron	$m_n = 1.674 \times 10^{-27}$ kg
Mass of a proton	$m_p = 1.672 \times 10^{-27}$ kg
Avogadro's number	$N_A = 6.0221367 \times 10^{23}$ mole^{-1}
Boltzmann's constant	$k = 1.380658 \times 10^{-23}$ J K^{-1}
Faraday's constant	$F = 9.6485309 \times 10^{4}$ C mole^{-1}
Fundamental unit charge	$e = 1.60217733 \times 10^{-19}$ C
Gas constant	$R = 8.314510$ J mole^{-1} K^{-1}
	= 0.08315 bar dm^3 mole^{-1} K^{-1}
	= 0.082058 L atm mole^{-1} K^{-1}
Heat capacity of water	$C = 4.184$ J g^{-1} K^{-1}
	= 75.4 J mole^{-1} K^{-1}
Planck's constant	$h = 6.6260755 \times 10^{-34}$ J s
Rydberg's constant	$R_H = 2.1798 \times 10^{-18}$ J
	$= 1.097 \times 10^{-2}$ nm^{-1}
Speed of light	$c = 2.99792458 \times 10^{8}$ m s^{-1}
Zero point	0°C = 273.15 K
K_w of H_2O at 25°C	$K_w = 1.00 \times 10^{-14}$
Pi	$\pi = 3.1415927$

CONVERSION FACTORS

1 atmosphere (atm) = 1.01325×10^{5} Pa (N m^{-2}) = 760.0 mm Hg (torr) = 1.01325 bar

1 calorie (cal) = 4.184 joules (J)

1 debye (D) = 3.335617×10^{-30} C m

1 eV/particle = 96.485 kJ mole^{-1} = 23.061 kcal mole^{-1}

1 eV = 1.602×10^{-19} J = 8067 cm^{-1}

1 kcal mole^{-1} = 4.184 kJ mole^{-1} = 349.73 cm^{-1}

1 kJ mole^{-1} = 0.23901 kcal mole^{-1} = 83.591 cm^{-1}

1 L atm = 101.325 J = 24.217 cal

$\ln x = 2.3026 \log x$

$$PV = nRT$$

$$P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$$

$\Delta U = q + w$

$dU = nC_{v,m}dT$

$H = U + PV$

$dH = nC_{p,m}dT$

$dw = -P_{ext}dV$

$$W_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT\ln\frac{V_2}{V_1} = -nRT\ln\frac{P_1}{P_2}$$

$\Delta H^\circ_{rxn} = \Sigma\upsilon_i * \Delta H^\circ_{f,i} + \Delta C_p * (T - 25°C)$

$\Delta C_p = \Sigma\upsilon_i * C_{p,i}$

For ideal gases, $C_{p,m} = C_{v,m} + R$

$$P_1V_1^\gamma = P_2V_2^\gamma \qquad \left(\frac{\bar{C}_P}{\bar{C}_V}\right) = \gamma$$

$$T_1V_1^{(\gamma-1)} = T_2V_2^{(\gamma-1)} \qquad T_1P_1^{[(1-\gamma)/\gamma]} = T_2P_2^{[(1-\gamma)/\gamma]}$$

Efficiency = $|w|/q_{in}$

$\varepsilon = 1 - T_C/T_H$

$$dS \equiv \frac{dQ_{reversible}}{T} \qquad \Delta S = nR\ln\frac{V_f}{V_i}$$

$$\Delta S^\circ(T_2) = \Delta S^\circ(T_1) + \int_{T_1}^{T_2} \Delta C_P \frac{dT}{T} \qquad \Delta S = nC_V\ln\frac{T_f}{T_i}$$

$$\Delta S^\circ = \sum coeff_p S^\circ(pdts) - \sum coeff_r S^\circ(rcts)$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \qquad \Delta S = nC_p\ln\frac{T_f}{T_i}$$

$$S = k\ln W$$

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$

$$\Delta G^\circ = \sum coeff_p \Delta G_f^\circ(pdts) - \sum coeff_r \Delta G_f^\circ(rcts)$$

$\Delta G^\circ = -RT\ln K$

$\Delta G_{rxn} = \Delta G_{rxn}^\varnothing + RT\ln(Q)$

$dG = VdP - SdT$

$$Q = \left[\frac{a_C^c a_D^d}{a_A^a a_B^b}\right]$$

$$\Delta P_1 = P_1^* x_2 \qquad P_1 = a_1 P_1^*$$

$$P_2 = K'm \qquad \Delta P_1 = a_2 P_1^*$$

$$\pi = MRT \qquad a_1 = \gamma x_1 \qquad a_2 = \gamma x_2$$

$S_{gas} = K_H P_{gas}$

$$\ln\left(\frac{K(T_1)}{K(T_2)}\right) = -\frac{\Delta H^\circ_{reaction}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}} \qquad \frac{dP}{dT} = \frac{P\Delta_{vap}\bar{H}}{RT^2}$$

First order reaction: $\ln\{[A]_o/[A]\} = kt$

Second order reaction: $1/[A] - 1/[A]_o = kt$

Zero order reaction: $[A] = -kt + [A]_o$

Arrhenius equation: $k = Ae^{-Ea/RT}$

$E = h\nu \qquad \lambda = c/\nu \qquad \lambda = h/mv$

$E_{photon} = h\nu_0 + E_k \qquad E_n = -R_H Z^2/n^2$

Particle in a 1D box $\quad E_n = \dfrac{n^2h^2}{8mL^2} \qquad \psi_n = \sqrt{\dfrac{2}{L}}\sin\dfrac{n\pi}{L}x$

$$-\log\frac{I}{I_0} = -\log T = A \qquad E_{rot} = \frac{J(J+1)h^2}{8\pi^2 I} \qquad \mu = \frac{m_1m_2}{m_1+m_2} \qquad I = \mu r^2$$

$$A = \varepsilon bc$$

$$E_{vib} = (v + \frac{1}{2})h\nu \qquad \frac{n_i}{n_j} = \frac{g_i}{g_j}e^{-(E_i-E_j)/k_BT}$$

PERIODIC TABLE OF THE ELEMENTS

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

GROUP NUMBERS IUPAC RECOMMENDATION (1985) — 13; GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986) — IIIA

ATOMIC NUMBER — 5; RELATIVE ATOMIC MASS (1) — 10.811; SYMBOL — B; ELEMENT NAME — BORON

PERIOD	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 (VIIIB)	9 (VIIIB)	10 (VIIIB)	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

PERIOD														
6	57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

PERIOD														
7	89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have 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@netlinx.com)

You may tear this sheet off