Name: ________________________ Student number: __________________________

Final Exam – CHM2130 – April 28, 2006

Prof. David Bryce – University of Ottawa

Total time available: 3 hours (9:30 am to 12:30 pm)
Suggested timing: 30 minutes per question x 6 questions = 3 hours

Instructions: Make sure you have all 13 pages. If you write in pencil, you cannot have any part of the exam considered for re-marking. If you need extra space, you may write on the backs of the pages, but indicate that you are doing so. You must answer all questions.

Show all work for full marks!!

Formula sheets: This is a **closed-book exam**. You are not allowed to bring in any of your own formula sheets, notes, books etc. A formula sheet is found on page 2, and some formulas are given in the questions.

Calculators: only non-programmable faculty-approved calculators are permitted.

Question	Mark received	Total possible mark
#1		/ 15
#2		/ 20
#3		/ 20
#4		/ 15
#5		/ 15
#6		/ 15
Total		/ 100

Best of luck on the exam, and best of luck in the future!
It has been my pleasure teaching you.

FORMULAS and FUNDAMENTAL CONSTANTS

$c = 2.99792458 \times 10^{8}$ m s^{-1} $N_A = 6.02214 \times 10^{23}$ mol^{-1} 0°C = 273.15 K
$k = 1.38065 \times 10^{-23}$ J K^{-1} $u = 1.66054 \times 10^{-27}$ kg
$R = 8.31447$ J K^{-1} mol^{-1} 1 J = 1 kg m^{2} s^{-2}
$h = 6.62608 \times 10^{-34}$ J s 1 N = 1 kg m s^{-2}
mass of electron = 9.10938×10^{-31} kg

$$\ln x! \approx x \ln x - x \qquad W = \frac{N!}{n_0!n_1!n_2!\cdots} \qquad q = \sum_j g_j e^{-\beta\varepsilon_j} \qquad \left(\frac{\partial \ln x}{\partial x}\right) = \frac{1}{x}$$

$$Q = \sum_i e^{-\beta E_i} \qquad S = k \ln W \qquad S = \frac{U - U(0)}{T} + k \ln Q$$

$$\nu_L = \frac{\gamma B_0}{2\pi} \qquad \Delta p \Delta x \geq \frac{1}{2}\hbar \qquad B = \frac{\hbar}{4\pi c I}$$

$$q = q^T q^R q^V q^E = \left(\frac{V}{\Lambda^3}\right)\left(\frac{kT}{\sigma hcB}\right)\left(\frac{1}{1 - e^{-\beta hc\tilde{\nu}}}\right)\left(g^E\right) \qquad \int \psi_n {}^*\psi_{n'} d\tau = 0$$

harmonic oscillator: $E_v = \left(v + \frac{1}{2}\right)\hbar\omega \qquad \omega = \sqrt{\frac{k}{m_{eff}}} \qquad v = 0, 1, 2, \ldots; \Delta v = \pm 1$

harmonic oscillator: $G(v) = \left(v + \frac{1}{2}\right)\tilde{\nu} \qquad \tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{m_{eff}}} \qquad v = 0, 1, 2, \ldots; \Delta v = \pm 1$

$\int \psi_n {}^*\psi_n d\tau = 1 \qquad \langle n|n'\rangle = \delta_{nn'}$ diatomic molecule: $\mu = m_{eff} = \dfrac{m_A m_B}{m_A + m_B}$

$$\Delta G = \Delta H - T\Delta S \quad H\psi = E\psi \quad p = h/\lambda \qquad \langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, d\tau \qquad \omega = 2\pi\nu$$

$$dx\,dy\,dz = r^2 dr \sin\theta \, d\theta \, d\phi \qquad \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} \qquad \hat{x} = x \times \qquad P \propto |\psi|^2 d\tau$$

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-Mv^2/2RT\right) \qquad E_J = hcBJ(J+1)$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \psi = \sum_k c_k \psi_k \qquad e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \ldots$$

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \cdots \qquad \langle \Omega \rangle = |c_1|^2 \omega_1 + |c_2|^2 \omega_2$$

$$\lambda\nu = c \qquad \tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \qquad \varepsilon_J = hc\bar{\nu}_J \quad E = h\nu \qquad PV = nRT \qquad N = nN_A \qquad Nk = nR$$

$$W' = N'(A + B'\rho) \qquad W_{net} = NB\rho - N'B'\rho = (N - N')B\rho$$

$$\tilde{\nu}_O(J) = \tilde{\nu}_i - \tilde{\nu} - 2B + 4BJ$$

$F(J,K) = BJ(J+1)$ with $J = 0, 1, 2, \ldots$

$$\tilde{\nu}_Q(J) = \tilde{\nu}_i - \tilde{\nu}$$

$$E(J, M_J) = hcBJ(J+1) + a(J, M_J)\mu^2 \mathcal{E}^2$$

$$\tilde{\nu}_S(J) = \tilde{\nu}_i - \tilde{\nu} - 6B - 4BJ$$

rotational transitions (symmetric or linear rotor):

$\Delta J = \pm 1$ and $\Delta M_J = 0$ or ± 1 $\quad \tilde{\nu}(J + 1 \leftarrow J) = 2B(J+1)$ with $J = 0, 1, 2, \ldots$

#1. **(15 MARKS total)** SHORT ANSWERS: You must answer all parts of this question.

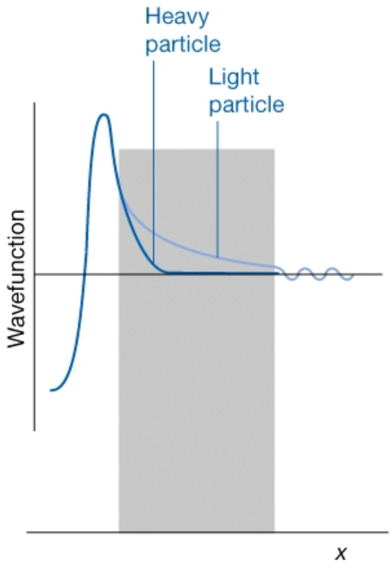
(a) **(2 marks)** Sketch the Maxwell distribution for a gas at two different temperatures. Indicate which curve corresponds to "high temperature" and which corresponds to "low temperature".

(b) **(1 mark)** In statistical thermodynamics, what is meant by the "dominating configuration"?

(c) **(1 mark)** What is Graham's empirical Law of effusion? (Do not simply describe effusion in general)

(d) **(1 mark)** In the discussion of blackbody radiation, what two quantities are related by Wien's displacement law?

(e) **(1 marks)** What quantum mechanical phenomenon is depicted in this figure?



(f) **(2 marks)** What is the Stark effect? Discuss in terms of the quantum number M_J.

(g) **(1 mark)** How many nodes does the wavefunction of the 4th excited state of a 1D particle in a box have?

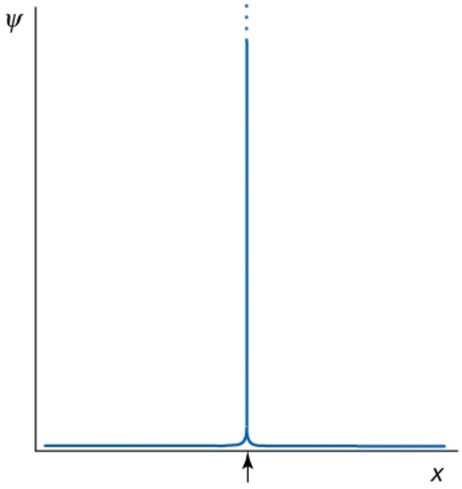
(h) **(2 marks)** For absorption spectroscopy of gaseous samples, name the two processes which result in a finite lifetime, τ, of the excited energy state.

(i) **(2 marks)** On the basis of the following equation, qualitatively sketch the y-component of nuclear spin magnetization as a function of time after a π/2 pulse. Here, $M_{0,y}$ is the initial magnetization along the *y* direction after the pulse.

$$M_y(t) = M_{0,y}\cos(2\pi\nu_L t)e^{-t/T_2}$$

(j) **(1 mark)** In which part of the electromagnetic spectrum do vibrational transitions appear?

(k) **(1 mark)** What can you say about a particle's (i) position and (ii) momentum from the diagram shown? What does the arrow denote?



#2. (20 MARKS Total)

The first-order decomposition reaction of a *cis*-azoalkane in an ethanol solution was monitored by the loss of nitrogen gas and the following rate constants (k_1) were recorded as a function of temperature:

T / °C	-24.82	-20.73	-17.02	-13.00	-8.95
k_1 / s^{-1}	1.22×10^{-4}	2.31×10^{-4}	4.39×10^{-4}	8.50×10^{-4}	14.3×10^{-4}

(a) **(18 marks)** Calculate the enthalpy of activation ($\Delta H^{\oplus}$), entropy of activation ($\Delta S^{\oplus}$), and Gibbs energy of activation ($\Delta G^{\oplus}$) at -20°C. Among other equations, you will need the following version of the Eyring equation, which applies to the current situation (first-order process in solution). Make a reasonable assumption regarding the transmission coefficient, κ. You will also need the fact that $\Delta H^{\oplus} = E_a - RT$ in solution.

$$k_1 = \kappa \frac{kT}{h} e^{-\Delta G^{\oplus}/RT}$$

If you make a graph, please *be careful about your choice of scale*. There is extra space on the next page.

(b) **(2 marks)** Comment on the result you obtain for the entropy of activation.

#3. (20 MARKS Total)
A graduate student noted the following lines in the pure rotational absorption spectrum of $^{1}H^{35}Cl$ (measured in cm^{-1}): 21.19, 42.37, 63.56, 84.75, 105.93, 127.12, 148.31. These correspond to the seven lowest-energy rotational transitions and were measured at 298.15 K. There are more lines in the spectrum but these are all the data the graduate student noted before leaving for a vacation. ($m(^{1}H) = 1.0078\ u$; $m(^{35}Cl) = 34.969\ u$; $m(^{37}Cl) = 36.9659\ u$)

(a) **(4 marks)** Deduce the value of the rotational constant for $^{1}H^{35}Cl$ and comment on the rigid rotor approximation in the context of the data presented.

(b) **(6 marks)** Calculate the rotational partition function for $^{1}H^{35}Cl$ at 25.0°C by explicit summation. Reminder: don't forget about degeneracy.

(c) **(4 marks)** Calculate the rotational partition function for $^{1}H^{35}Cl$ at 25.0 °C using the following approximate formula. Explain why the result agrees or disagrees with the result you obtained in (b). Here, B is the rotational constant and σ is the symmetry number.

$$q^R \approx \frac{kT}{\sigma hcB}$$

(d) **(6 marks)** Derive a general expression (for a heteronuclear diatomic molecule) for the value of the quantum number J which corresponds to the most highly populated energy level (J_{max}). Verify that your result successfully predicts which term contributes the most to the rotational partition function which you calculated in part (b).

#4. (15 MARKS Total) Suppose that the wavefunction for a system is:

$$\Psi(x) = \frac{1}{2}\psi_1(x) + \frac{1}{4}\psi_2(x) + \frac{3+\sqrt{2}\,i}{4}\psi_3(x)$$

and that ψ_1(x), ψ_2(x), and ψ_3(x) are normalized eigenfunctions of the kinetic energy operator, with eigenvalues E_1, $3E_1$, and $7E_1$, respectively.

(a) **(6 marks)** Verify that Ψ(x) is normalized. Show all work for full marks.

(b) **(3 marks)** What are the possible values you could obtain in measuring the kinetic energy on a large number of identical systems described by this total wavefunction? (Express your answers as a function of E_1.)

(c) **(3 marks)** What is the probability of measuring each of the values you identified in part (b)?

(d) **(3 marks)** What is the average value of the kinetic energy (or expectation value) that you would obtain from a large number of measurements? Express your answer as a function of E_1.

#5. (15 MARKS Total) Recall that the Einstein coefficients for stimulated emission (B') and stimulated absorption (B) are equal to each other and that the Einstein coefficient for spontaneous emission (A) is given by $8B\pi h\nu^3/c^3$. Suppose the ratio of A to B' is found to be 1.70506 x 10^{-16} J s m^{-3} for vibrational transitions in $^{12}C^{16}O$. ($m(^{12}C)$ = 12.0000 u ; $m(^{13}C)$ = 13.0034 u ; $m(^{16}O)$ = 15.9949 u ; $m(^{17}O)$ = 16.99913 u)

(a) **(10 marks)** Find the vibrational wavenumber and force constant (k) for $^{13}C^{16}O$ (an isotopomer of $^{12}C^{16}O$). You may assume that the force constant is independent of isotopic substitution, and that the harmonic approximation is valid.

(b) **(5 marks)** Draw an energy level diagram which shows only the transitions corresponding to the **S branch of the anti-Stokes line** allowed in the vibrational Raman spectroscopy of a heteronuclear diatomic molecule such as carbon monoxide. Show at least 5 allowed transitions.

#6. **(15 MARKS Total)**

(a) **(10 marks)** Two ^{15}N nuclei (spin ½) have chemical shifts of 1.2 ppm and 2.4 ppm and a $J(^{15}\text{N}, ^{15}\text{N})$ coupling constant of 27.6 Hz. Do these nuclei form an A_2, AX or an AB spin system if (i) $B_0 = 4.7$ T; (ii) $B_0 = 21.1$ T? The magnetogyric ratio of ^{15}N is 2.7126×10^7 T^{-1} s^{-1}.

(b) **(5 marks)** What has the NMR operator done during the time between the situation shown below at left, and the situation shown below at right? Draw a third set of cones representing the situation after a π pulse (180 degree pulse) has been applied to the set of cones shown at right.