Name: ________________________ Student number: __________________________

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Final Exam – CHM2330 – April 28, 2008

Prof. David Bryce – University of Ottawa

Total time available: 3 hours (2:00 pm to 5:00 pm)

Instructions: Make sure you have all 15 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. Formulas are found on pages 2 and 3, and some formulas are given in the questions.

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

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

$c = 2.99792458 \text{ x } 10^{8}$ m s^{-1} $\quad N_A = 6.02214 \text{ x } 10^{23}$ mol^{-1} $\quad 0°\text{C} = 273.15$ K
$k = 1.38065 \text{ x } 10^{-23}$ J K^{-1} $\quad u = 1.66054 \text{ x } 10^{-27}$ kg $\quad \hbar = h/2\pi$
$R = 8.31447$ J K^{-1} mol^{-1} $\quad$ 1 J = 1 kg m^{2} s^{-2} $\quad \beta = 1/kT$
$h = 6.62608 \text{ x } 10^{-34}$ J s $\quad$ 1 N = 1 kg m s^{-2} $\quad$ 1 Pa = 1 kg m^{-1}s^{-2}
$m(^{12}\text{C}) = 12.0000\ u$; $m(^{13}\text{C}) = 13.0034\ u$; $m(^{16}\text{O}) = 15.9949\ u$; $m(^{17}\text{O}) = 16.99913\ u$
$m(^{1}\text{H}) = 1.0078\ u$; $m(^{35}\text{Cl}) = 34.9688\ u$; $m(^{37}\text{Cl}) = 36.9651\ u$
mass of electron = $9.10938 \text{ x } 10^{-31}$ kg $\quad \gamma(^{13}\text{C}) = 6.728284 \text{ x } 10^{7}$ T^{-1} s^{-1} $\quad$ 1 dm = 10^{-1}m

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

$$q^R = \sum_J (2J+1)e^{-\beta hcBJ(J+1)} \qquad q^R \approx \frac{kT}{\sigma hcB} \qquad \left(\frac{\partial \ln x}{\partial x}\right) = \frac{1}{x}$$

$$Q = \sum_i e^{-\beta E_i} \qquad S = k \ln W \qquad S = \frac{U - U(0)}{T} + k \ln Q \qquad \int \frac{1}{x} dx = \ln x + \text{constant}$$

$$PV = nRT \qquad \nu_L = \frac{\gamma B_0}{2\pi} \qquad \Delta p \Delta x \geq \frac{1}{2}\hbar \qquad B = \frac{\hbar}{4\pi c I} \qquad I = \sum_i m_i r_i^2$$

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

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

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

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

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

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

$$\int_0^\infty \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx = \frac{4\pi^4}{15} \qquad k = Ae^{-\frac{E_a}{RT}}$$

$$\psi = \sum_k c_k \psi_k \qquad \left[\hat{\Omega}_1, \hat{\Omega}_2\right] = \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1$$

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \ldots \qquad \int \sin^2(ax) dx = \frac{1}{2}x - \frac{1}{4a}\sin(2ax) + constant$$

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \cdots \qquad \langle\Omega\rangle = |c_1|^2\omega_1 + |c_2|^2\omega_2 \qquad A = \left(\frac{8\pi h\nu^3}{c^3}\right)B$$

$$\lambda\nu = c \qquad \tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \qquad \varepsilon_J = hc\bar{\nu}_J \quad E = h\nu \qquad PV = nRT \qquad N = nN_{\mathrm{A}}$$

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

$$\tilde{\nu}_P(J) = S(v+1, J-1) - S(v,J) = \tilde{\nu} - 2BJ$$
$$\tilde{\nu}_Q(J) = S(v+1, J) - S(v,J) = \tilde{\nu}$$
$$\tilde{\nu}_R(J) = S(v+1, J+1) - S(v,J) = \tilde{\nu} + 2B(J+1)$$

$$\tilde{\nu}_O(J) = \tilde{\nu}_i - \tilde{\nu} - 2B + 4BJ$$
$$\tilde{\nu}_Q(J) = \tilde{\nu}_i - \tilde{\nu}$$
$$\tilde{\nu}_S(J) = \tilde{\nu}_i - \tilde{\nu} - 6B - 4BJ$$

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

$$a(J,M_J) = \frac{J(J+1) - 3M_J^2}{2hcBJ(J+1)(2J-1)(2J+3)}$$

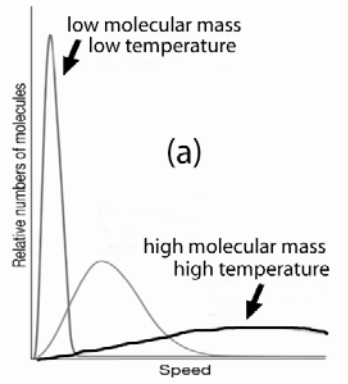
$$\left|\mu_{J+1,J}\right|^2 = \left(\frac{J+1}{2J+1}\right)\mu_0^2 \qquad G - G(0) = -kT\ln Q + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

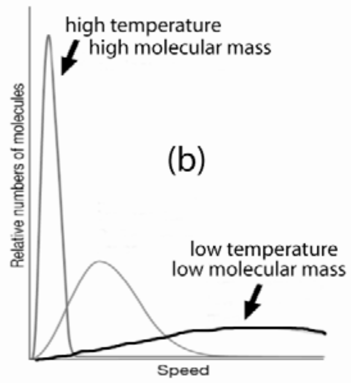
$$\left\langle \varepsilon^M \right\rangle = -\frac{1}{q^M}\left(\frac{\partial q^M}{\partial \beta}\right)_V \qquad M = T, R, V, E$$

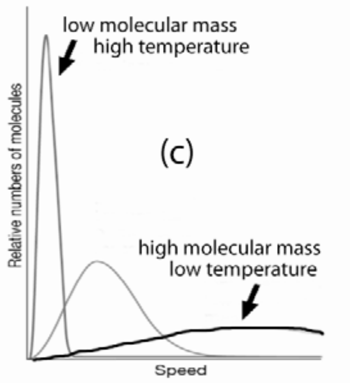
for distinguishable independent molecules, $Q = q^{\mathrm{N}}$
for indistinguishable independent molecules, $Q = q^{\mathrm{N}} / \mathrm{N}!$

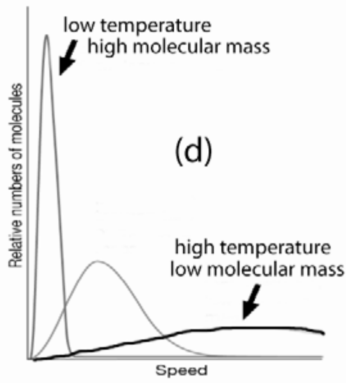
#1. **(20 MARKS total)** SHORT ANSWERS: You must answer all parts of this question.

(a) (1 mark) In which example(s) are all four labels correct for the Maxwell distribution?









(b) (2 marks) What is the ultraviolet catastrophe?

(c) (2 marks) What is the wavelength of a baseball which weighs 145 g when it is thrown at 140 km per hour?

(d) (2 marks) The speed of an electron is known to within 1.0 μm s^{-1}. What is the minimum uncertainty in the position of the electron?

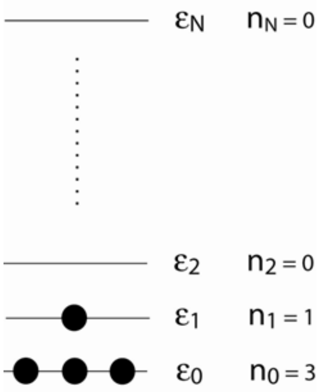
(e) (1 mark) If Ω_1 and Ω_2 are **complementary observables** corresponding to the operators $\hat{\Omega}_1, \hat{\Omega}_2$, what can you say about the **commutator** of these two operators?

(f) (1 mark) What is the ***zero-point energy*** for a harmonic oscillator?

(g) (2 marks) Name the two sources of line broadening for spectroscopy of gaseous samples.

(h) (1 mark) What is the gross selection rule for rotational Raman spectroscopy?

(i) (1 mark) What is the configuration of the system shown in the Figure?



(j) (2 marks) Evaluate the rotational partition function of $^{12}C^{16}O$ at 225°C, given that $B = 1.9313\ cm^{-1}$.

(k) (2 marks) Find the integrated form of this first-order rate law: $\frac{d[A]}{dt} = -k[A]$

(l) (1 mark) Simplify the following rate expression (for the Lindemann-Hinshelwood mechanism) in the limit where $k_a'[A] << k_b$.

$$\frac{d[P]}{dt} = \frac{k_a k_b [A]^2}{k_b + k_a^{'}[A]}$$

(m) (2 marks) What are the two types of explosions we discussed in class?

(n) (0 marks) Take a deep breath and relax.

#2. STATISTICAL THERMODYNAMICS **(20 MARKS total)**

(a) (10 marks) Derive the ideal gas law ($PV = nRT$) for indistinguishable independent molecules starting from the statistical-thermodynamic expression for pressure.

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

(b) (5 marks) Given the Boltzmann distribution (below), find the relative populations of the states of a two-level system when the temperature approaches infinity.

$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

(c) (5 marks) A molecule has a non-degenerate excited state lying at 540 cm^{-1} above a non-degenerate ground state. At what temperature will 10% of the molecules be in the upper state?

#3. KINETICS AND REACTION DYNAMICS **(20 MARKS total)**

(a) (10 marks) The rate of the decomposition of ethanol was measured over the temperature range 700-1000 K, and the rate constants are reported below. Find the activation energy E_a and the pre-exponential factor A. Be careful with units!

T (K)	700	760	790	840	910	1000
k_2 ($dm^3\ mol^{-1}\ s^{-1}$)	0.011	0.105	0.343	2.17	20.0	145

(b) (10 marks) Using the following relations and the value of *A* you determined in part (a), find the entropy of activation, $\Delta S^{\oplus}$ at 790 K.

$p^{\Theta} = 100\text{kPa}$.

$E_a = \Delta H^{\oplus} + 2RT$

$$k_2 = \kappa \frac{kT}{h} \frac{RT}{p^{\Theta}} e^{-\Delta G^{\oplus}/RT}$$

#4. QUANTUM THEORY **(20 MARKS total)**

(a) (10 marks) 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 $\psi_1(x)$, $\psi_2(x)$, and $\psi_3(x)$ are normalized eigenfunctions of the kinetic energy operator, with eigenvalues E_1, $3E_1$, and $7E_1$, respectively.

Verify that $\Psi(x)$ is normalized or not. Show all work for full marks.

(b) (5 marks) Referring to part (a), 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.

(c) (5 marks) This part is independent of parts (a) and (b). The Debye formula for heat capacity is given below. Find a simplified version of the Debye formula which applies only at ***low temperature***.

$$C_{V,m} = 3Rf \qquad where\ f = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\left(e^x - 1\right)^2} dx$$

#5. SPECTROSCOPY **(20 MARKS total)**

(a) (3 marks) Here is a vibrational-rotational spectrum of HCl in the gas phase. Label, on the spectrum, the three different branches which are shown. Indicate clearly which spectral region corresponds to which branch.

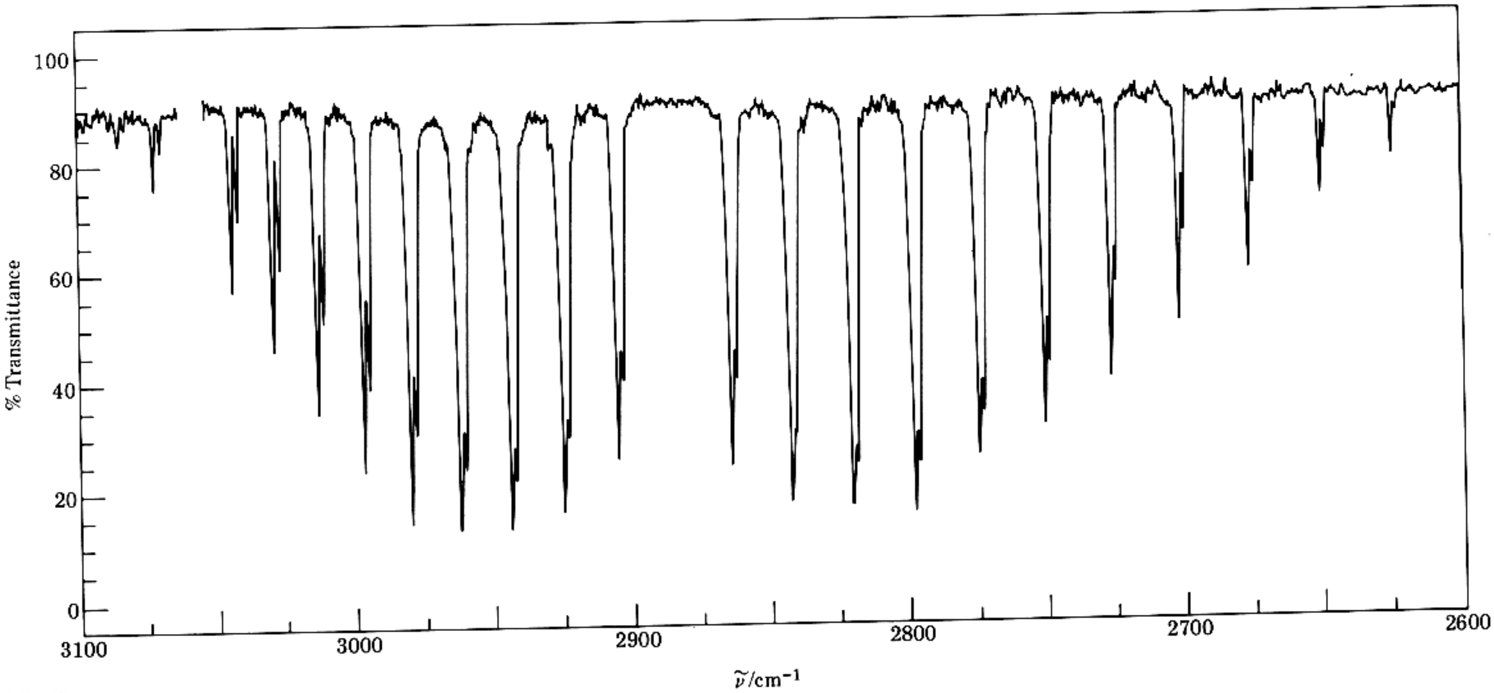


Figure 25.1 Vibration–rotation spectrum of HCl. (Courtesy Prof. Raj Khanna, University of Maryland.)

(b) (2 marks) From the spectrum, estimate the rotational constant for HCl.

(c) (6 marks) Determine the bond length in $^{1}H^{35}Cl$.

(d) (5 marks) This part is independent of parts (a), (b), (c). In NMR spectroscopy, what is the difference between an AX and an AB spin system? What is the minimum value of the *J* coupling constant required to have an AX system when the chemical shifts of the two coupled nuclei (^{13}C) are -2 and 21 ppm in a magnetic field of 4.7 T?

(e) (4 marks) This part is independent of parts (a), (b), (c), (d). Given the wavefunctions and energies for a particle in a 3D box (below), what is the degeneracy of the first excited state when the box is a cube?

$$\psi_{n_1,n_2,n_3}(x,y,z) = \sqrt{\frac{8}{L_1 L_2 L_3}}\,\sin\left(\frac{n_1 \pi x}{L_1}\right)\,\sin\left(\frac{n_2 \pi y}{L_2}\right)\,\sin\left(\frac{n_3 \pi z}{L_3}\right)$$

$$E_{n_1,n_2,n_3} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)\frac{h^2}{8m}$$