Name: ________________________ Student number: __________________________

uOttawa

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Final Exam – CHM2330 – April 14, 2009
Prof. David Bryce – University of Ottawa

Total time available: 3 hours (9:30 am to 12:30 pm)

Instructions: Make sure you have all 14 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		/ 18
#2		/ 8
#3		/ 8
#4		/ 8
#5		/ 8
#6		/ 5
#7		/ 5
Total		/ 60

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

for distinguishable independent molecules, $Q = q^N$
for indistinguishable independent molecules, $Q = q^N / N!$

#1. **(18 MARKS TOTAL)** SHORT ANSWERS: You must answer all parts of this question.

(a) (1 mark) According to the Maxwell distribution of speeds of molecules in a gas, will nitrogen molecules or hydrogen molecules have a broader probability distribution (at a fixed temperature)?

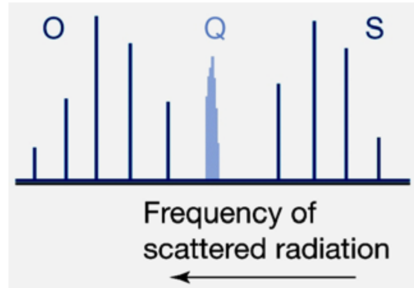
(b) (1 mark) How many nodes are there in the wavefunction corresponding to the 3^{rd} excited state of a particle in a 1D box?

(c) (1 mark) In which part of the electromagnetic spectrum do rotational transitions appear?

(d) (3 marks) Name the three contributions to transitions between different energy states identified by Einstein.

(e) (1 mark) What is the difference between a symmetric rotor and an asymmetric rotor?

(f) (1 mark) What type of spectrum is shown?



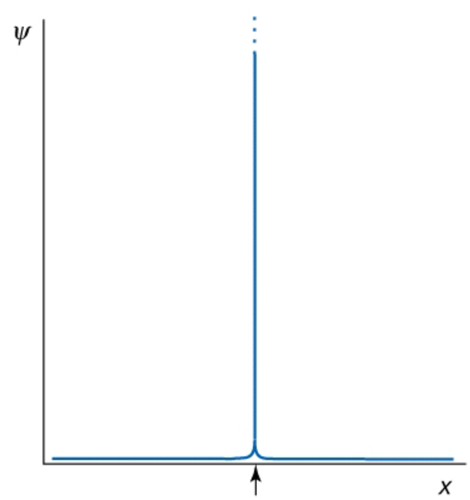
(g) (2 marks) In the vibrational spectroscopy of diatomic molecules, what are overtone lines and why are they not strictly forbidden?

(h) (4 marks) Underline the molecules which may show a pure rotational absorption spectrum; circle the molecules which may show a pure rotational Raman spectrum. Assume the rigid rotor approximation is valid.

H_2 HCl CH_4

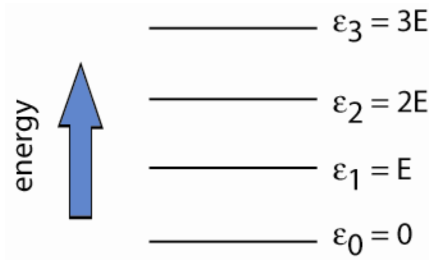
(i) (1 mark) What are the two types of explosions we discussed in class?

(j) (2 marks) What can you say about a particle's (i) position and (ii) momentum from the diagram shown?



(k) (1 mark) Which 'mode of motion' contributes to the heat capacity of isolated atoms?

#2. **(8 MARKS TOTAL)** Suppose you have a system consisting of three molecules. Shown below are the first four energy levels of the system. The energy of level 1 is equal to an arbitrary amount "E". The energy of level two is equal to "2E" and the energy of level three is equal to "3E".



(a) (1 marks) Name a system we discussed in class which is similar to this one. Explain why.

(b) (3 marks) Suppose the total energy of the system must be 5E. How many different distinguishable distributions of the three ***distinguishable molecules*** over the four energy levels can there be? Draw all possible distributions.

number of distinguishable distributions: [ ]

(c) (1 marks) What is the weight, *W*, of the dominating configuration?

(d) (3 marks) Now, assuming that E = 1.00 x 10^{-21} J and that each of the levels is four-fold degenerate, what is value of the partition function (q) for this system at 25°C?

partition function: | q = |

#3. (8 MARKS TOTAL) In class we saw the Lindemann-Hinshelwood mechanism in the context of a unimolecular isomerization reaction, $A \rightarrow P$. Suppose we have an ideal gas of "A" molecules. The first elementary step in the reaction is:

$$A + A \xrightarrow{k_a} A^* + A$$

where A* is a vibrationally-excited molecule of "A".

(a) (1 mark) Write the rate law for the above elementary reaction.

d[A*]/dt =

(b) (3 marks) We saw that after generating A*, there are two possible subsequent steps. Either the product P is formed (an isomer of A), or A* relaxes and two molecules of A are regenerated. Fill in the rate laws for each of these elementary reactions.

$$A^* + A \xrightarrow{k_a'} A + A$$

d[A*]/dt =

$$A^* \xrightarrow{k_b} P$$

d[A*]/dt = and d[P]/dt =

(c) (1 mark) Combine the three contributions to d[A*]/dt to write a rate law for the overall reaction:

d[A*]/dt =

(d) (2 marks) Apply the *steady state approximation* to A* and determine the overall rate law in terms of d[P]/dt.

d[P]/dt =

(e) (1 mark) Suppose the concentration of A is low, so that k_a'[A] << k_b, and simplify the expression you obtained in part (d). Your answer should be quite simple!

#4. (8 MARKS TOTAL) The solutions to the one-dimensional particle-in-a-box problem are, for $0 \le x \le L$:

$$E_n = \frac{n^2 h^2}{8mL^2} \quad ; \quad \psi_n(x) = \sqrt{\frac{2}{L}}\sin(n\pi x / L) \qquad n = 1,2,\cdots$$

where L is the length of the box, h is Planck's constant, n is the quantum number, m is the mass of the particle.

(a) (2 marks) Find the zero-point energy for an electron in a box of length 1.0 nm.

(b) (2 marks) Show that the wavefunction is normalized (or not).

(c) (2 marks) Find the energy required to excite the electron from its first excited state to its second excited state in the same 1D box of length 1.0 nm.

(d) (2 marks) What is the probability, P, of locating an electron between $x = 0$ and $x = 0.2$ nm in its lowest energy state in a box of length 1.0 nm?

#5. (8 MARKS TOTAL)

(a) (4 marks) The rotational Raman spectrum of $^{19}F_2$ has a series of Stokes lines separated by 3.5312 cm^{-1}. Calculate the bond length of the molecule. The mass of ^{19}F is 18.9984 u.

(b) (4 marks) Draw an energy level diagram for the first five rotational states of $^{19}F_2$. Label the levels with quantum numbers. Indicate the energies of each of the levels (i.e., report numbers with correct units). Draw an arrow representing one possible transition which would appear in the Stokes part of the spectrum, and one possible transition which would appear in the anti-Stokes part.

#6. (5 MARKS TOTAL)

Two ^{31}P nuclei (spin ½) have chemical shifts of -11.0 ppm and 31.0 ppm and a $J(^{31}P, ^{31}P)$ coupling constant of 284 Hz.
The magnetogyric ratio of ^{31}P is 10.8394 x 10^7 rad T^{-1} s^{-1}.

(a) (2 marks) Calculate the Larmor frequency of ^{31}P in a magnetic field (B_0) of 21.1 T.

(b) (2 marks) Do these nuclei form an AX or an AB spin system if B_0 = 21.1 T? Show your work.

(c) (1 mark) Is ^{31}P a boson or a fermion?

#7. (5 MARKS TOTAL)

(a) (2 marks) Calculate the commutator of the position and momentum operators.

(b) (1 mark) Comment on your result in the context of Heisenberg's uncertainty principle. (Or if you were not able to answer part (a), comment on Heisenberg's uncertainty principle in general.)

(c) (2 marks) The speed of an electron is known to within 1.1 x 10^{-7} m s^{-1}. What is the minimum uncertainty in the position of the electron?