

Chemistry 430/530a Practice

Midterm 2

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Problem 1.1.

$$Q(N, V, E) = \Omega$$

$$k_B T = 200 \text{ cm}^{-1}, 0.6 \text{ kcal/mol}, 2.5 \text{ kJ/mol}$$

(at $T=293\text{K}$, any unit system)

$$Q(N, V, T) = \sum_j e^{-\beta E_j}$$

$$S(p_j) = -k_B \sum_j p_j \ln p_j$$

For a heteronuclear diatomic molecule:

$$H_{\text{trans}} = \frac{p^2}{2m}$$

$$E_{\text{trans}} = \frac{h^2 (n_x^2 + n_y^2 + n_z^2) / 8mL^2}$$

$$q_{\text{trans}} = \frac{(2\pi m k_B T / h^2)^{3/2} L^3}{\text{(can substitute } V=L^3)}$$

$$H_{\text{vib}} = \frac{p^2}{2m} + \frac{1}{2} k x^2 \text{ or } \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

$$E_{\text{vib}} = h\omega(n + \frac{1}{2})$$

$$q_{\text{vib}} = \frac{(1 - e^{-\Theta_{\text{vib}}/T})^{-1} \text{ or } e^{-\Theta_{\text{vib}}/2T} (1 - e^{-\Theta_{\text{vib}}/T})^{-1}}{\text{if ZPE is included in } q_{\text{elec}}; \Theta_{\text{vib}} = h\omega/k_B}$$

$$H_{\text{rot}} = \frac{L^2}{2I} = \frac{L^2}{2\mu r^2}$$

$$E_{\text{rot}} = B J(J+1), B = h^2 / 8\pi^2 I_c$$

$$q_{\text{rot}} = \sum_j (2J+1) e^{-B J(J+1)/kT} \text{ or } \sum_j (2J+1) e^{-\Theta_{\text{rot}} J(J+1)/T}; \Theta_{\text{rot}} = \frac{h^2}{8\pi^2 I_c k_B}$$

$$q_{\text{elec}} = \sum_n g_n e^{-E_n/k_B T} \approx g_0 + g_1 e^{-E_1/k_B T} + g_2 e^{-E_2/k_B T}$$

Problem 1.2. Deuterium, $D = {}^2\text{H}$, has a nuclear spin of $I = 1$. For molecular deuterium, the ground electronic state is Σ_g^+ . Given the degeneracy rules:

$$g_I = (2I + 1)(I + 1) \quad \text{symmetric (ortho) nuclear spin states}$$

$$g_I = (2I + 1)I \quad \text{anti-symmetric (para) nuclear spin states,}$$

write the rotational partition functions for the para and ortho states as a sum over rotational energy levels. Use this to approximate the ratio of ortho:para populations as $T \rightarrow 0\text{K}$ and at $T \approx 300\text{K}$.

Since the nuclei are bosons $\Psi_{\text{tot}} = \rho_{12} \Psi_{\text{tot}}$

$$\frac{\Psi_{\text{tot}}}{\text{even}} = \frac{\Psi_{\text{elec}}}{\text{even}} \times \frac{\Psi_{\text{rot}}}{\substack{J=1,3,\dots \text{ odd} \\ J=0,2,\dots \text{ even}}} \times \frac{\Psi_{\text{nuc.sp}}}{\substack{(2 \cdot 1 + 1)(1 + 1) = 6 \text{ even states} \\ (2 \cdot 1 + 1) \cdot 1 = 3 \text{ odd states} \\ (\text{even} \times \text{even} \text{ or } \text{odd} \times \text{odd})}}$$

$$q_{\text{rot,ortho}} = \sum_{J=0,2,4,\dots} 6(2J+1) e^{-J(J+1)\theta_r/T}$$

$$q_{\text{rot,para}} = \sum_{J=1,3,5,\dots} 3(2J+1) e^{-J(J+1)\theta_r/T}$$

As $T \rightarrow 0\text{K}$, only $J=0$ populated $\rightarrow 100\%$ ortho

As $T \gg \theta_r$, 6:3 ratio of ortho:para \rightarrow 67% ortho
33% para

($\theta_r = 44\text{K}$, but you don't need this
to know that rotational modes
are in the high T limit at 300K)

Problem 1.3. Given that

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} \quad (1)$$

$$C_V = -k\beta^2 \frac{\partial \langle E \rangle}{\partial \beta} \quad (2)$$

show that if the energy eigenvalues of a system can be expressed as a sum of independent contributions ($E = E_A + E_B + E_C$), then the heat capacity can also be expressed as a sum of independent contributions ($C_V = C_{V,A} + C_{V,B} + C_{V,C}$).

We have been approximating molecular vibrations as harmonic oscillators ($n \in \{0, 1, 2, \dots\}$, an infinite set) although they are often better described as Morse oscillators (for example N_2 , $\omega = 2331 \text{ cm}^{-1}$, may only have about 30 bound levels). Use your result above to explain why the harmonic oscillator is a fair approximation at room temperature.

$$Q = \sum_{A,B,C} e^{-\beta(E_A + E_B + E_C)} = \left(\sum_A e^{-\beta E_A} \right) \left(\sum_B e^{-\beta E_B} \right) \left(\sum_C e^{-\beta E_C} \right) = q_A q_B q_C$$

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = -\left(\frac{\partial \ln q_A}{\partial \beta} + \frac{\partial \ln q_B}{\partial \beta} + \frac{\partial \ln q_C}{\partial \beta} \right)$$

$$C_V = k\beta^2 \left(\frac{\partial^2 \ln q_A}{\partial \beta^2} + \frac{\partial^2 \ln q_B}{\partial \beta^2} + \frac{\partial^2 \ln q_C}{\partial \beta^2} \right)$$

$$= C_{V,A} + C_{V,B} + C_{V,C}$$

(Ignore part 2 - not representative of The midterm.)

Problem 1.4.

In this problem we consider the changes upon condensation of N argon atoms in the canonical ensemble. How many rotational, translational, and vibrational modes does the system have as a vapor? Derive, or write down, the heat capacity and average energy for argon in the vapor phase.

○ rotational, 0 vibrational, $3N$ translational D.O.F.

$$C_V \approx \frac{3Nk_B}{2}$$

$$\langle E \rangle \approx \frac{3Nk_B T}{2}$$

(always in high T limit for translations)

Now the N argon atoms have been condensed into a solid that exists in a vacuum. Depending on the structure of the cluster, each atom could have a coordination number of 12 (hexagonal close packed), 8 (body-centered cubic), or 6 (simple cubic). Make any assumption you need to about the bonding to write down how many rotational, translational, and vibrational modes the system has. Assuming this solid is in the high temperature limit, write down or derive the heat capacity and average energy.

Assume that all atoms in the cluster are bound;
That is, not free to translate without affecting
the energy of the entire cluster.

3 rotational, 3 translational, $3N-6$ vibrational D.O.F.

$$C_V \approx \frac{6k_B}{2} + (3N-6)k_B = (3N-3)k_B$$

$$\langle E \rangle \approx (3N-3)k_B T$$

A high-school student you are tutoring wants to know why the specific heat of water approximately doubles from 1.9 to $4.2 \frac{\text{kJ}}{\text{kgK}}$ for a vapor and liquid at the same temperature, and simply cannot understand how rearranging the atoms while keeping the same number of degrees of freedom should change the heat capacity at all. Write 2-3 short sentences explaining this without any math. (Continue on back if needed.)

Heat capacity describes how well a material can store thermal energy. More chemical bonds formed means more places to store energy and a higher heat capacity. (Like a towel vs. a long thread.)

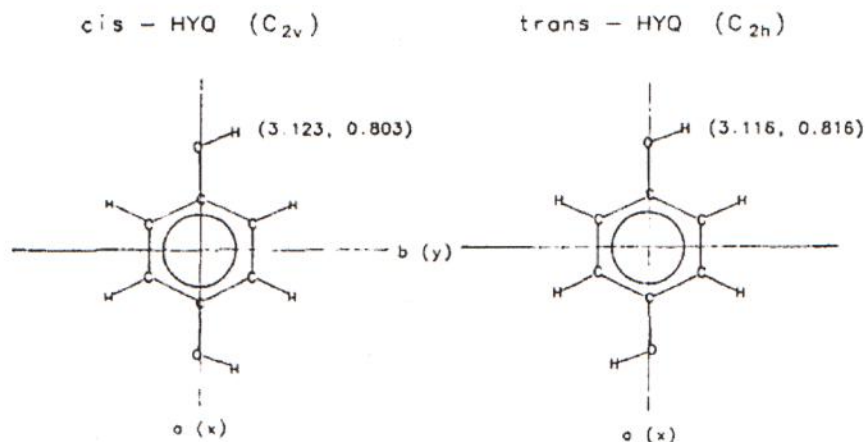


FIG. 1. The *cis* and *trans* rotamers of hydroquinone. (x,y) denote the 6-31G* coordinates of the hydroxy-hydrogen atoms in the ground state.

Figure used with permission, SJ Humphrey and DW Pratt, J. Chem. Phys. 99(7), 1993

Problem 1.5. The figure above shows the *cis*- and *trans*- rotamers of hydroquinone. If you had two pure samples, each consisting of one of these rotamers, which experiment could you use to distinguish between the two? What observable would you look for and how would you analyze it?

In *cis*-HYQ, the b -axis rotations exchange all identical nuclei. (For ^{16}O , ^{12}C , ^1H , this means 6 fermions are exchanged.)

In *trans*-HYQ, the c -axis rotations exchange all identical nuclei.

Since this is an asymmetric top ($I_a \neq I_b \neq I_c$),

Spin statistics will affect different frequency rotational modes for each rotamer.

Fit a measure of the rotational spectrum and look for the peak splitting for the modes affected by intensity alternation - match this to either the b - or c -axis rotational constant.