

Chemistry 430/530a Practice

Midterm 2

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Problem 1.1.

$$Q(N, V, E) = \underline{\hspace{4cm}}$$

$$k_B T = \underline{\hspace{4cm}}$$

(at $T=293K$, any unit system)

$$Q(N, V, T) = \underline{\hspace{4cm}}$$

$$S(p_j) = \underline{\hspace{4cm}}$$

For a heteronuclear diatomic molecule:

$$H_{trans} = \underline{\hspace{4cm}}$$

$$E_{trans} = \underline{\hspace{4cm}}$$

$$q_{trans} = \underline{\hspace{4cm}}$$

$$H_{vib} = \underline{\hspace{4cm}}$$

$$E_{vib} = \underline{\hspace{4cm}}$$

$$q_{vib} = \underline{\hspace{4cm}}$$

$$H_{rot} = \underline{\hspace{4cm}}$$

$$E_{rot} = \underline{\hspace{4cm}}$$

$$q_{rot} = \underline{\hspace{4cm}}$$

$$q_{elec} = \underline{\hspace{4cm}}$$

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:

$g_I = (2I + 1)(I + 1)$ symmetric (ortho) nuclear spin states

$g_I = (2I + 1)I$ 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 $T \approx 300\text{K}$.

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.

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.

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.

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.)

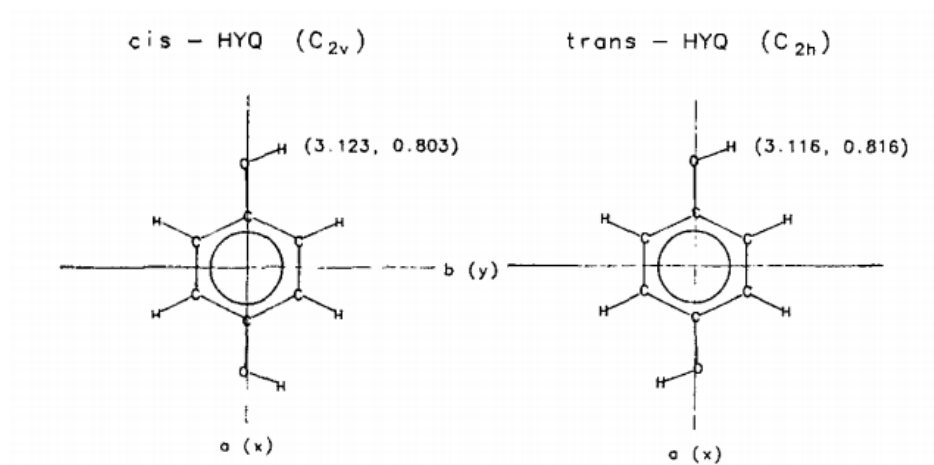


FIG. 1. The *cis* and *trans* rotamers of hydroquinone. (x,y) denote the 6-31G* coordinates of the hydroxy-hydrogen atoms in the ground state.

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?