

S3. The atmosphere closely obeys the Boltzmann distribution. This math is exactly the same as $K = \exp(-\Delta G^0/RT)$; (it is referred to as the Gibbs-Boltzmann relation by Wikipedia). Here we use ΔU instead of ΔG^0 because entropy and pV work are not significant effects in this problem. For this problem $K = p(\text{altitude } 2)/p(\text{altitude } 1)$, i.e., the ratio of pressures at any two altitudes.

Using the Boltzmann distribution, find the atmospheric pressure (bars) in a place whose **elevation = 12,345 feet** above sea level), assuming $T=298$ K. Assume the degeneracy (**which is the W in $S=k_B \ln W$**) is effectively a constant for altitudes below 100,000 ft. Use the average molecular mass of the air molecules, which is $0.2(32) + 0.8(28) = 28.8$ g/mol. (remember that the ratio of the pressures is the ratio of concentrations).

S4. From the Boltzmann distribution, find the ratio of probabilities to be in the first excited vibrational quantum state compared to being in the lowest (zero-point) state for **N_2 and I_2** gases, given that for **N_2** , the vibrational energy level spacing is about **28.5 kJ/mole**, but for **I_2** the energy of the vibrational energy level spacing is only **2.55 kJ/mol**. How do your results show that it is reasonable that the vibrational degrees of freedom do not contribute significantly to heat capacity for **N_2** but they do for **I_2** . (The degeneracy of vibrational states = 1).

Below is not a problem, but is a summary of what is on page 24 about: Equipartition of Energy and Heat Capacities. Rereading *p. 24* you will find that a molecule soaks up $\frac{1}{2} k_B T$ J per each molecular "degree of freedom", i.e., $\frac{1}{2} RT$ J/mol per degree of freedom. All molecules have 3 translational degrees of freedom, and diatomic molecules have two rotational degrees of freedom at room temperature. They also have 1 vibration (which gives 2 more degrees, 1 kinetic energy and 1 for potential energy). This would seem to predict molar energies of $7/2 RT$, and therefore $C_{v,m} = 7/2 R$ and $C_{p,m} = 9/2 R$, but at room temperature most diatomics have $C_{v,m}$ close to $5/2 R$ and therefore $C_{p,m}$ close to $7/2 R$. This seemingly inexplicable behavior is understandable from a combination of the **Boltzmann distribution** combined with the basic result of **quantum mechanics of the harmonic oscillator**: Later in the semester you will learn that the vibrational quantum energy level spacing is proportional to the vibrational frequency, and is given by $\Delta E = h\nu_{\text{vib}}$. Strong bonds between low mass atoms have high vibrational frequencies and therefore a larger energy jump to reach the excited vibrational states. (Just for your further information (but not needed to work this problem), the vibrational energy level spacing = $h\nu_{\text{vib}}$. ν_{vib} for $N_2 = 2358.6 \text{ cm}^{-1}$; ν_{vib} for I_2 is 208 cm^{-1} ; the difference is because N is a light atom and N-N bond is a very strong triple bond. I_2 has a very weak single bond and the atoms are much heavier.)

Exam 2 is on Friday, October 12, 7:55-8:55 am in the usual meeting room. It is closed book and over chapters 3,4, plus p. 24 of Chapter 2 and p. 162 of Chapter 5, which are pertinent to this homework. You may have one 4 x 6" sheet of handwritten information (both sides) of your choosing for use on the exam.