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Collaborators

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Problem 1

Cold Interstellar molecular clouds often contain the molecule cyanogen (CN) whose first rotational excited states have an energy of $\epsilon_0 = 4.7 \times 10^{-4}$ eV above the ground state. In 1941, studies revealed that starlight passing through these molecular clouds showed that 29 percent of the CN molecules are in the first excited rotational state. To account for this data, astronomers suggested that the CN molecules might be in thermal equilibrium with a reservoir at a well defined temperature.

a) The energy of the rotational state with angular momentum $j(j = 0, 1, 2, \dots)$ is given by $\epsilon(j) = \epsilon_0 j(j + 1)/2$, and the degeneracy of the level (i.e. number of states with the same energy) is $\Omega(j) = 2j + 1$. Note that the ground state has $j = 0$. Find an expression for the temperature of the thermal reservoir as a function of the fraction x of the excited CN molecules. For simplicity, neglect occupation of states with $j > 1$

   Solution: First, we can calculate $\langle E \rangle$ in terms of the fraction of ionized energy:

   $$\langle E \rangle = \epsilon_0 x$$

   Calculating the partition function:

   $$Z = 1 + 3e^{-\epsilon_0/k_B T}$$

   Then, we can come up with an expression for the probability of being in the first excited state:

   $$P(j = 1) = \frac{3e^{-\epsilon_0/k_B T}}{1 + 3e^{-\epsilon_0/k_B T}} = \frac{3}{e^{\epsilon_0 \beta} + 3}$$

   Then, since x is the fraction of excited molecules, this is also equal to the probability of the particles being in the excited state, so we can just set this equal to x. Then, we can simplify:

   $$\frac{3}{e^{\epsilon_0 \beta} + 3} = x \implies T = \frac{\epsilon_0}{k_B \ln\left(\frac{3}{x} - 3\right)}$$

   $\square$

b) Evaluate your answer from part (a) to find the temperature corresponding to the observed excited fraction. What do you think is the origin of the thermal radiation with which the CN molecule is in equilibrium?

   Solution: Plugging $x = 0.29$ into this equation gives a temperature $T = 2.73$ K. The reason it has this temperature is likely due to the residual heat of the CMB, which is responsible for the "ambient temperature" of the universe. $\square$

c) Justify the assumption made in (a), that all the molecules are either in the ground or first excited state (Hint: Using your temperature from part (b), compute the fraction of molecules that will be in the second excited state.)

Solution: To calculate this quantity, we first need to modify the partition function to admit the second energy level:

$$Z = 1 + 3e^{-\epsilon_0\beta} + 5e^{-3\epsilon_0\beta}$$

Therefore, the probability of being in the second state is:

$$P(j = 2) = \frac{5e^{-3\epsilon_0\beta}}{Z} = 0.0087$$

This means that the probability is 0.8%, so we are justified in our assumption that $j > 1$ states aren't occupied.
□

Schroeder 7.5

Consider a system consisting of a single impurity atom/ion in a semiconductor. Suppose that the impurity atom has one "extra" electron compared to the neighboring atoms, as would a phosphorous atom occupying a lattice site in a silicon crystal. The extra electron is then easily removed, leaving behind a positively charged ion. The ionized electron is called a **conduction electron**, because it is free to move through the material; the impurity atom is called a **donor**, because it can "donate" a conduction electron. This system is analogous to the hydrogen atom considered in the previous two problems except that the ionization energy is much less, mainly due to the screening of the ionic charge by the dielectric behavior of the medium.

a) Write down the formula for the probability of a single donor atom being ionized. Do not neglect the fact that the electron, if present, can have two independent spin states. Express your formula in terms of the temperature, the ionization energy I, and the chemical potential of the "gas" of ionized electrons.

   Solution: Recall that the probability is calculated as:

$$P(s) = \frac{1}{Z} e^{-(E(s) - \mu N(s))/kT}$$

   For the sake of simplicity, let the ionized state have energy 0 and $N = 0$, and the ground state will have energy $-I$ and $N = 1$. With this in mind, our partition function is:

$$Z = 1 + 2e^{-(-I-\mu)/kT} = 1 + 2e^{(I+\mu)/kT}$$

   Therefore, the probability of being in the excited state is:

$$P(\text{ionized}) = \frac{1}{1 + e^{(I+\mu)/kT}}$$

   □

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b) Assuming that the conduction electrons behave like an ordinary ideal gas (with two spin states per particle), write their chemical potential in terms of the number of conduction electrons per unit volume, N_c/V.

   Solution: Following the example given in the textbook, we can use Equation 6.93:

$$\mu = -kT \ln\left(\frac{V Z_{\text{int}}}{N v_Q}\right)$$

   To calculate Z_{int}, we calculate the partition function over the spin state energies. However, since they have the same energy, we can just set them equal to zero, and since there are two spin states, we have $Z_{\text{int}} = 2$ as a result. Therefore:

$$\mu = -kT \ln\left(\frac{2V}{N_c v_Q}\right)$$

   Here, the v_Q refers to the quantum volume, so it's defined as:

$$v_Q = \ell_Q^3 = \left(\frac{h}{\sqrt{2\pi m k T}}\right)^3$$

   □

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c) Now assume that every conduction electron comes from an ionized donor atom. In this case the number of conduction electrons is equal to the number of donors that are ionized. Use this condition to derive a quadratic equation for N_c in terms of the number of donor atoms (N_d), eliminating μ. Solve for N_c using

the quadratic formula. (Hint: It's helpful to introduce some abbreviations for dimensionless quantities. Try $x = N_c/N_d$, $t = kT/I$, and so on.)

Solution: We calculate N_c/N_d in part (a) when we're calculating the probability of being ionized, so therefore we can just set them equal to each other:

$$\frac{N_c}{N_d} = \frac{1}{1 + 2e^{(I+\mu)/kT}}$$

From here, we can calculate μ using the equation we derived in the previous part, and eventually getting us the following quadratic equation:

$$N_c^2 \left(\frac{e^{1/t} v_Q}{V} \right) + N_c - N_d = 0$$

Solving this quadratic gives the solution:

$$N_c = \frac{\sqrt{1 + 4N_d \frac{e^{1/t} v_Q}{V}} - 1}{\frac{2e^{1/t} v_Q}{V}}$$

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d) For phosphorous in silicon, the ionization energy is 0.044 eV. Suppose that there are 10^{17} P atoms per cubic centimeter. Using these numbers, calculate and plot the fraction of ionized donors as a function of temperature. Discuss the results.

Solution: After a lot of screwing around in Mathematica, I got the following function, where N_c/N_d is on the y-axis and t is on the x-axis:
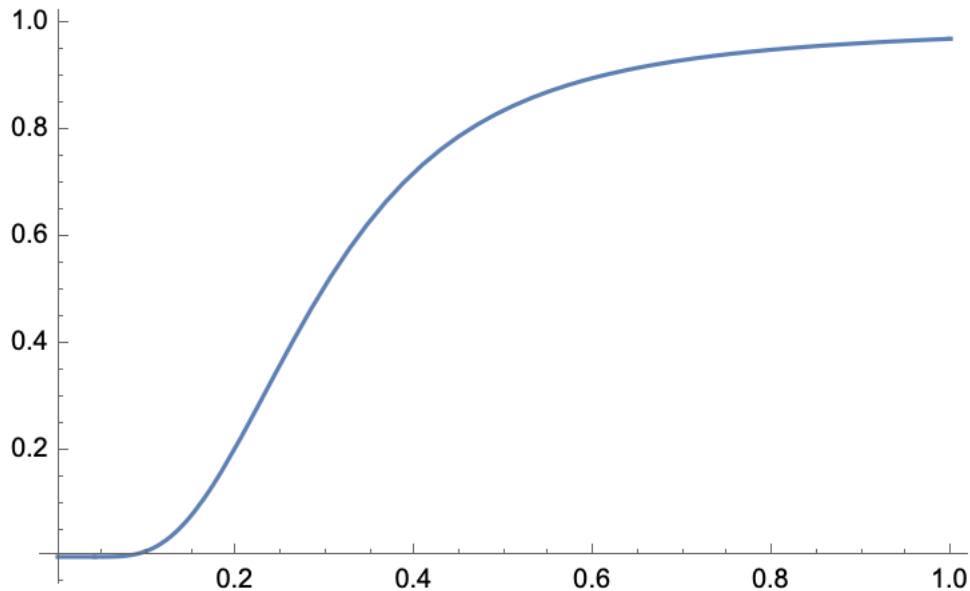

A bit of analysis: $t = \frac{kT}{I}$, so increasing t is proportional to increasing T. Therefore, we can see that as temperature increases, a larger fraction of the phosphorous atoms are ionized, which matches our intuition about what we intuitively expect to happen at high temperatures. We also see that it becomes almost completely ionized when $I = kT$, which makes sense, since this corresponds to a situation where almost all of the electrons in phosphorous are at or above the ionization energy.

Also, the plot has a horizontal asymptote at 1 since we're plotting a ratio of ionized atoms. ☐

Schroeder 5.83

Write down the equilibrium condition for each of the following reactions:
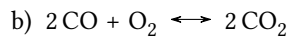
a) $2\,H \longleftrightarrow H_2$
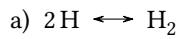
Solution: As explained in the textbook, we just replace the $\longleftrightarrow$ by an equality, and replace the species by their chemical potentials. Therefore, this is:

$$2\mu_H = \mu_{H_2}$$

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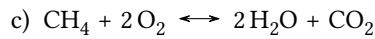b) $2\,CO + O_2 \longleftrightarrow 2\,CO_2$

Solution: Same thing:

$$2\mu_{CO} + \mu_{O_2} = 2\mu_{CO_2}$$

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c) $CH_4 + 2\,O_2 \longleftrightarrow 2\,H_2O + CO_2$

Solution: And again..

$$\mu_{CH_4} + 2O_2 = 2\mu_{H_2O} + \mu_{CO_2}$$

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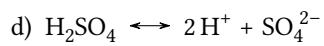
d) $H_2SO_4 \longleftrightarrow 2\,H^+ + SO_4^{2-}$

Solution: Typing is hard…

$$\mu_{H_2SO_4} = 2\mu_{H^+} + \mu_{SO_4^{2-}}$$

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e) $2\,p + 2\,n \longleftrightarrow {}^4He$
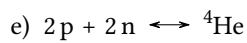
Solution: Last one!

$$2\mu_p + 2\mu_n = \mu_{He}$$

☐

Schroeder 5.84

A mixture of one part nitrogen and three parts hydrogen is heated, in the presence of a suitable catalyst, to a temperature of $500°$ C. What fraction of the nitrogen (atom for atom) is converted to ammonia, if the final total pressure is 400 atm? Pretend for simplicity that the gases behave ideally despite the very high pressure. The equilibrium constant at $500°C$ is 6.9×10^{-5}. (Hint: You'll have to solve a quadratic equation.)

Solution: The problem statement gives us that the final pressure is 400 atmospheres, so we know that

$$P_{H_2} + P_{N_2} + P_{NH_3} = 400$$

Then, since we have 3 parts hydrogen for each 1 part nitrogen, then we also have:

$$P_{H_2} = 3P_{N_2}$$

Finally, we use the law of mass action:

$$K = \frac{P_{NH_3}^2 (P°)^2}{P_{N_2} P_{H_2}^3}$$

Then, since $P°$ is the background atmosphere (which is 1 in atmospheres), this then simplifies to:

$$P_{NH_3} = \sqrt{27K} P_{H_2}^2$$

Substituting this back into the first equation gives us our quadratic equation:

$$4P_{N_2} + \sqrt{27K} P_{N_2}^2 = 400$$

Solving this quadratic using Mathematica, we get $P_{N_2} = 60.50$, so we also get $P_{H_2} = 181.505$ and $P_{NH_3} = 157.994$. Finally, the ratio of the pressures gives a relationship between the fraction of reacted molecules, so we have to divide the partial pressure of ammonia with the partial pressure of nitrogen (we have to multiply the nitrogen by 2 since there are 2 particles in nitrogen):

$$\frac{P_{NH_3}}{2P_{N_2}} = 1.31 \approx \frac{4}{3}$$

Therefore, the fraction of ammonia that gets converted is given by:

$$\frac{N_{NH_3}}{N_{NH_3+N_{N_2}}} = \frac{4}{4+3} = \frac{4}{7}$$

so we have $\frac{4}{7}$ of the molecules are converted into ammonia. □

Schroeder 5.85

Derive the **van't Hoff equation**,

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

which gives the dependence of the equilibrium constant on temperature. Here ΔH° is the enthalpy change of the reaction, for pure substances in their standard states (1 bar pressure for gases). Notice that if ΔH° is positive (loosely speaking, if the reaction requires the absorption of heat), then higher temperature makes the reaction tend more to the right, as you might expect. Often you can neglect the temperature dependence of ΔH° ; solve the equation in this case to obtain

$$\ln K(T_2) - \ln K(T_1) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Solution: We have the equation that:

$$e^{-\Delta G/RT} = K \implies \ln K = -\frac{\Delta G}{RT}$$

Therefore, now we can take the derivative:

$$\frac{\partial \ln K}{\partial T} = -\frac{1}{R}\frac{\partial \Delta G}{\partial T}$$

We can then do this via quotient rule, since ΔG is also a function of T:

$$\frac{\partial \ln K}{\partial T} = -\frac{1}{RT^2}\left[T\frac{\partial \Delta G}{\partial T} - \Delta G\right]$$

$$= \frac{1}{RT^2}\left[T(-\Delta S) - (\Delta H - T\Delta S)\right]$$

$$= \frac{\Delta H}{RT^2}$$

In the first to second line, I've used the property that $\frac{\partial \Delta G}{\partial T} = -\Delta S$ from the thermodynamic identities. For the second part of the problem, we basically just have to solve a differential equation:

$$d\ln K = \Delta\frac{H}{RT^2}dT$$

And now we can integrate both sides of this equation from T_1 to T_2. Note that the problem tells us that ΔH is independent of T, so we can pull it out of the integral:

$$\int_{T_1}^{T_2} d\ln K = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{1}{T^2}dT$$

$$(\ln K)_{T_1}^{T_2} = \frac{\Delta H}{R}\left(-\frac{1}{T}\right)_{T_1}^{T_2}$$

Then, we can substitute the limits in, use logarithm rules to get:

$$\ln K(T_2) - \ln K(T_1) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

as desired. $\square$