

T6B.1:

$$\frac{1}{T} = \frac{\partial S}{\partial U} \approx \frac{\Delta S}{\Delta U}$$

$$T \approx \frac{\Delta U}{\Delta S} = \frac{35 \text{ J}}{0.1 \text{ J/K}} = 350 \text{ K}$$

T6B.5: According to Eq. T6.32 the energy levels of the orbiting electron in the H-atom are given by:

$$E_n = \frac{-13.6 \text{ eV}}{n^2}$$

where  $n = 1$  is the ground state and  $n = 2$  is the first excited state. So  $\Delta E = -13.6/4 + 13.6 = 10.2 \text{ eV}$ .

$$\frac{\Pr(E_2)}{\Pr(E_1)} = e^{-\Delta E/kT} = \exp\left(\frac{-10.2 \cdot 1.6022 \times 10^{-19}}{1.3807 \times 10^{-23} \cdot 9500}\right) = 3.88 \times 10^{-6}$$

where I've used the conversion factor:  $1.6022 \times 10^{-19} \text{ J/eV}$ . As discussed on p. 107 there are actually four  $n = 2$  states ( $2s, 2p_x, 2p_y, 2p_z$ ), each one of which would have the above probability, so the total probability of all  $n = 2$  states is  $4 \times 3.88 \times 10^{-6} = 1.55 \times 10^{-5}$  FYI: this fraction is small but quite measurable—about  $3000\times$  the similar fraction in the Sun.

T6S.4: Note:  $S = k \ln(\Omega) = k(N \ln V + \frac{3}{2}N \ln U + \text{constant})$

$$\frac{1}{T} = \frac{\partial S}{\partial U} = k \frac{\partial \ln \Omega}{\partial U} = \frac{3}{2}Nk \frac{\partial \ln U}{\partial U} = \frac{\frac{3}{2}Nk}{U}$$

$$U = \frac{3}{2}NkT$$

T6S.7:  $E_n = \hbar\omega \left(n + \frac{1}{2}\right)$ , for  $n = 0, 1, 2, \dots$

$$Z = \sum_{n=0}^{\infty} \exp(-E_n/kT) = \exp(-\hbar\omega/2kT) \sum_{n=0}^{\infty} \exp(-\hbar\omega n/kT)$$

This series can actually be exactly summed as it is geometric: define  $r = \exp(-\hbar\omega/kT)$ , then:

$$Z = \sqrt{r} \sum_{n=0}^{\infty} r^n = \frac{\sqrt{r}}{1-r} = \frac{1}{1/\sqrt{r} - \sqrt{r}} = \frac{1}{2} \frac{2}{\exp(+\hbar\omega/2kT) - \exp(-\hbar\omega/2kT)} = \frac{1}{2} \frac{1}{\sinh(\hbar\omega/2kT)}$$

I'll take "room temperature" to be  $20^\circ\text{C} = 293 \text{ K}$ , in which case:

$$\hbar\omega/kT = \frac{1.0546 \times 10^{-34} \cdot 3 \times 10^{14}}{1.3807 \times 10^{-23} \cdot 293} = 7.8207$$

$$\Pr(E_n) = \frac{e^{-E_n/kT}}{Z} = e^{-E_n/kT} \cdot (2 \sinh(\hbar\omega/2kT))$$

$$\Pr(E_0) = e^{-.5 \cdot 7.8207} \cdot (2 \sinh(7.8207/2)) = 0.9995986$$

$$\Pr(E_1) = e^{-1.5 \cdot 7.8207} \cdot (2 \sinh(7.8207/2)) = 0.0004012$$

$$\Pr(E_2) = e^{-2.5 \cdot 7.8207} \cdot (2 \sinh(7.8207/2)) = 1.61 \times 10^{-7}$$

Note: approximation of  $Z$  by adding three terms:

$$Z = \frac{1}{2 \sinh(\hbar\omega/2kT)} = \frac{1}{2 \sinh(7.8207/2)} = 2.00415 \times 10^{-2}$$

$$= \sqrt{r} \sum_{n=0}^{\infty} r^n \quad \text{where: } r = \exp(-\hbar\omega/kT) = \exp(-7.8207) = .00040134$$

$$\approx 2.00335 \times 10^{-2} (1 + .00040134 + 1.61 \times 10^{-7}) = 2.00335 \times 10^{-2} (1.00040150) = 2.00415 \times 10^{-2}$$

Boltzmann\_Factor.problems.txt

A. The Boltzmann factor is:

$$\frac{N_1}{N_0} = e^{-\Delta E/kT}$$

For HCl:

$$\frac{\Delta E}{kT} = \frac{.37 \cdot 1.6022 \times 10^{-19}}{1.3807 \times 10^{-23} \cdot 298} = 14.4$$

$$\frac{N_1}{N_0} = e^{-14.4} = 5.53 \times 10^{-7}$$

For I<sub>2</sub>:

$$\frac{\Delta E}{kT} = \frac{.027 \cdot 1.6022 \times 10^{-19}}{1.3807 \times 10^{-23} \cdot 298} = 1.05$$

$$\frac{N_1}{N_0} = e^{-1.05} = 0.349$$

Only I<sub>2</sub> is vibrationally excited so (at this temperature) only it would have additions to  $f$  for vibrations.