

## Solutions to Homework Problem Set 18

### Stowe 15.22

In this problem, the relevant energy is the gravitational potential energy. The stratification of the atmosphere is such that the density and therefore pressure gradient of the atmosphere balances the weight of the atmosphere. From another point of view, we may treat the atmosphere at different altitude with a different gravitational potential energy with Boltzmann distribution, and the air density is proportional to the probability (or fraction of the number of air particles) at that altitude. The question is, therefore, to find the ratio of the number of air particles at altitude  $h$  and to the number of particles at altitude 0. The gravitational potential energy for an air particle at altitude  $h$  is  $mg(h + R)$ , where  $R$  is the radius of Earth, and the gravitational potential energy for the particle at sea level is  $mgR$ , if  $g$  is assumed to be a constant over the range of  $h$ . Therefore,  $\rho(h)/\rho(0) = e^{-\epsilon(h)/kT}/e^{-\epsilon(0)/kT} = e^{-[\epsilon(h)-\epsilon(0)]/kT} = e^{-[mg(h+R)-mgR]/kT} = e^{-mgh/kT}$ . If this ratio is  $1/2$ , then  $e^{-mgh/kT} = 0.5$ , leading to  $h = kT \ln 2 / mg = 5.4 \times 10^3 \text{ m}$ . So at about 5 km above the sea level, the air density is half that at sea level.

### Stowe 15.33

(a) we evaluate the exponent in the Boltzmann factor by equating  $\epsilon = kT$  to find the excitation temperature. For the vibrational excitation,  $\epsilon_{vib} = 0.2 \text{ eV}$ , so  $T_{vib} = \epsilon_{vib}/k = 2.3 \times 10^3 \text{ K}$ .

(b) According to the expression of the quantized rotational energy  $\epsilon_{rot} = 1/(2I)l(l+1)\hbar^2$ , the first excited rotational energy is  $\epsilon_{rot}(l=1) = \hbar^2/I$ , so the excitation temperature is  $T_{rot} = \epsilon_{rot}/k = \hbar^2/I/k = 8.1 \text{ K}$ .

(c) At room temperature of  $10^2 \text{ K}$ , the vibrational states are not excited, but the rotational states are. So rotational and translational energies will contribute to the specific heat. The translational motion has 3 degrees of freedom, and the rotational motion for this molecule also has 3 degrees of freedom (see discussion in class). According to equipartition, the mean energy in each degree of freedom contributes to  $1/2 R$  molar heat capacity, so altogether the molar heat capacity of this gas is  $1/2 R \times 6 = 3R$ .

### Reif 6.6

(a) At very low temperature, particles stay in the low-energy state, so the mean energy per particle is close to  $\epsilon_1$ . At high temperatures, there is nearly equal probability for particles to be in any available energy state, so the mean energy per particle is close to the mean of the two energies  $\frac{1}{2}(\epsilon_1 + \epsilon_2)$ . In between, a higher temperature raises the probability of high energy state relative to the probability of low energy state, so the mean energy increases with the temperature monotonically. As a thumb rule, the switch between the two limits is roughly when the probability of  $\epsilon_2$  is about  $1/e$  of the probability of  $\epsilon_1$ , or  $T \approx (\epsilon_2 - \epsilon_1)/k$ .

(b) According to (a), at both low and high temperatures, the heat capacity  $C_V$  is low, as the change

of the mean energy with temperature is gradual. Around the switching temperature, the  $C_V$  can have a peak indicating the sharp rise of the mean energy with temperature.

(c)

$$E(T) = N \frac{P_1 \epsilon_1 + P_2 \epsilon_2}{P_1 + P_2} = N \frac{\epsilon_1 e^{-\frac{\epsilon_1}{kT}} + \epsilon_2 e^{-\frac{\epsilon_2}{kT}}}{e^{-\frac{\epsilon_1}{kT}} + e^{-\frac{\epsilon_2}{kT}}} = N \frac{\epsilon_1 + \epsilon_2 e^{-\frac{\epsilon_2 - \epsilon_1}{kT}}}{1 + e^{-\frac{\epsilon_2 - \epsilon_1}{kT}}}$$

At the low temperature limit when  $(\epsilon_2 - \epsilon_1) \gg kT$ , the exponential function approaches zero, thus  $E(T) \approx N\epsilon_1$ . At very high temperatures when  $(\epsilon_2 - \epsilon_1) \ll kT$ ,  $e^{-(\epsilon_2 - \epsilon_1)/kT} \approx 1$ , thus  $E(T) \approx N(\epsilon_1 + \epsilon_2)/2$ .

$$C_V = \partial E(T)/\partial T)_V = Nk \left( \frac{\epsilon_2 - \epsilon_1}{kT} \right)^2 \frac{e^{-\frac{\epsilon_2 - \epsilon_1}{kT}}}{(1 + e^{-\frac{\epsilon_2 - \epsilon_1}{kT}})^2}$$

At the low temperature limit, the exponential function approaches zero faster than the growth of the  $[(\epsilon_2 - \epsilon_1)/kT]^2$  term, thus  $C_V \approx 0$ . At the high temperature limit, the exponential function takes the value of 1, thus

$$C_V \approx \frac{Nk}{4} \left( \frac{\epsilon_2 - \epsilon_1}{kT} \right)^2$$

which is inversely proportional to  $T^2$  and approaches zero when  $kT \gg \epsilon_2 - \epsilon_1$ .  $C_V$  peaks at the temperature  $T_p$  at which  $\partial C_V/\partial T = 0$ , yielding that  $\frac{\epsilon_2 - \epsilon_1}{kT_p} \approx 2.4$ .  $T_p$  is the temperature at which  $E(T)$  increases rapidly from its low temperature limit to high temperature limit.