MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Physics Department

8.044 Statistical Physics I — Spring Term 2013

Solutions to Problem Set #5

Problem 1: Correct Boltzmann Counting

a)

$$\begin{aligned}\Phi &= V^N\left[\frac{4\pi emE}{3N}\right]^{3N/2} \\ &= V^N\left[2\pi emkT\right]^{3N/2} \qquad \text{using } E=(3/2)NkT \\ S(N,V,T) &= k\ln\Phi \\ &= k\ln\left\{V^N\left[2\pi emkT\right]^{3N/2}\right\} \\ &= \underline{Nk\ln V+(3/2)Nk\ln[2\pi emkT]}\end{aligned}$$

Now let $N\to\lambda N$, $V\to\lambda V$, and $T\to T$. Then as a result

$$S\to\underbrace{\lambda Nk\ln(\lambda V)}_{\neq\lambda Nk\ln V}+\lambda(3/2)Nk\ln[2\pi emkT].$$

So $S\not\to\lambda S$ because of the failure in the first term.

b) The pressure is the same on both sides of the partition, so

$$P=\frac{N_1kT}{V_1}=\frac{N_2kT}{V_2}.$$

Now make use of the definition of α.

$$\frac{N_1kT}{\alpha V}=\frac{N_2kT}{(1-\alpha)V}$$

We can solve this to put N_1 and N_2 in terms of α.

$$\begin{aligned}N_2 &= \frac{1-\alpha}{\alpha}N_1 \\ \frac{N_1}{N_1+N_2} &= \frac{N_1}{(1+\frac{1-\alpha}{\alpha})N_1}=\underline{\alpha=\frac{N_1}{N}} \\ \frac{N_2}{N_1+N_2} &= \frac{N_2}{(\frac{\alpha}{1-\alpha}+1)N_2}=\underline{1-\alpha=\frac{N_2}{N}}\end{aligned}$$

Since the mixing takes place isothermally (because for ideal gases there is no interaction between the molecules), the T term in our expression for S of each gas does not change.

$$\begin{aligned}
\Delta S_1 &= N_1 k \ln V - N_1 k \ln \alpha V \\
&= N_1 k \ln(1/\alpha) = \underline{Nk\alpha \ln(1/\alpha)} \\
\Delta S_2 &= N_2 k \ln V - N_2 k \ln[(1-\alpha)V] \\
&= N_2 k \ln(1/1-\alpha) = \underline{Nk(1-\alpha)\ln(1/1-\alpha)} \\
\Delta S_1 + \Delta S_2 &= Nk[\underbrace{\alpha}_{+}\underbrace{\ln(1/\alpha)}_{+} + \underbrace{(1-\alpha)}_{+}\underbrace{\ln(1/1-\alpha)}_{+} \quad > 0
\end{aligned}$$

This result is correct if the two gases are different. What should we expect when the gases are the same? $\Delta E = 0$ since the internal energy of an ideal gas does not depend on the volume, $E(T,V) = E(T)$, and the initial and final temperatures are equal. $\Delta W = 0$ since no work is necessary to slide the partition in and out (there is no opposing force in the absence of friction). Using these two results in the first law, $\Delta E = \Delta W + \Delta Q$, tells us that $\Delta Q = 0$. If the process is reversible $\Delta S = \Delta Q/T$ and it follows that $\Delta S = 0$. This is not consistent with the detailed calculation above which indicated a positive ΔS, but which nowhere required that the two gases be different.

c)

$$\begin{aligned}
\Phi &= \frac{V^N}{N!}[2\pi emkT]^{3N/2} \\
S(N,V,T) &= Nk\ln V - Nk\ln N \qquad \underbrace{+kN}_{\substack{\text{neglect compared to} \\ \text{previous term}}} \qquad +(3/2)Nk\ln[2\pi emkT] \\
&= Nk\ln(V/N) + (3/2)Nk\ln[2\pi emkT]
\end{aligned}$$

Now let $N \to \lambda N$, $V \to \lambda V$, and $T \to T$.

$$S \to \lambda Nk\ln(V/N) + \lambda(3/2)Nk\ln[2\pi emkT] = \lambda S$$

We can summarize the results for the volume-dependent part of the entropies when the mixing involves only one gas by constructing a table.

VOLUME-DEPENDENT TERM IN THE ENTROPY			
	WITH PARTITION		WITHOUT PARTITION
OLD S	$\alpha Nk\ln\alpha V+(1-\alpha)Nk\ln(1-\alpha)V$ $=Nk[\alpha\ln\alpha V+(1-\alpha)\ln(1-\alpha)V]$ $=Nk[\underbrace{\alpha\ln\alpha+(1-\alpha)\ln(1-\alpha)}_{+}+\ln V]$	$\neq$	$Nk\ln V$
NEW S	$\alpha Nk\ln\frac{\alpha V}{\alpha N}+(1-\alpha)\ln\frac{(1-\alpha)V}{(1-\alpha)N}$ $=Nk[\alpha\ln(V/N)+(1-\alpha)\ln(V/N)]$ $=Nk\ln(V/N)$	$=$	$Nk\ln(V/N)$

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