6. *Statistical Mechanics and Thermodynamics* (Spring 2005)

A closed container is divided by a wall into two equal parts (A and B), each of volume $V/2$. Part A contains an ideal gas with $N/2$ molecules of mass M_1 while part B contains an ideal gas with $N/2$ molecules of mass M_2. The container is kept at a fixed temperature T. The molecules of each kind are all identical, but distinguishable from the molecules of the other kind.

(a) The partition function $Z(N)$ of an ideal gas of N particles of mass M in a volume V is given by

$$Z(N) = \frac{1}{N!}\left(\frac{V}{\sqrt{2\pi\hbar^2/Mk_BT}}\right)^N$$

Give the partition function of the gas in the container before and after the wall is removed. What are the entropy and pressure before and after the wall is removed?

(b) How much heat is absorbed or released following the removal of the wall? Is the removal of the wall a reversible or irreversible process?

(c) Same question as (b), but now for the case that the two kinds of molecules are indistinguishable from each other (so $M_1 = M_2$). Compare your answers for (b) and (c) and provide a physical explanation for the difference in entropy between the two cases.

a. Before: $Z_0(N) = \sum_r e^{-\beta E_r} \cong \int\cdots\int e^{-\beta E_r}\, dx_1^{(1)}\cdots dx_{N/2}^{(1)} dp_1^{(1)}\cdots dp_{N/2}^{(1)} dx_1^{(2)}\cdots dx_{N/2}^{(2)} dp_1^{(2)}\cdots dp_{N/2}^{(2)}$

$= \int\cdots\int e^{-\beta E_r^{(1)}} dx_1^{(1)}\cdots dx_{N/2}^{(1)} dp_1^{(1)}\cdots dp_{N/2}^{(1)} \int\cdots\int e^{-\beta E_r^{(2)}} dx_1^{(2)}\cdots dx_{N/2}^{(2)} dp_1^{(2)}\cdots dp_{N/2}^{(2)}$

$= Z_1(\frac{N}{2}) Z_2(\frac{N}{2}) = \frac{1}{(\frac{N}{2}!)(\frac{N}{2}!)}\left(\frac{V^2/4}{2\pi\hbar^2/\sqrt{M_1M_2}KT}\right)^{N/2}$

After the partition is removed, the only difference is the volume doubles.

After: $Z_0'(N) = \frac{1}{(\frac{N}{2}!)(\frac{N}{2}!)}\left(\frac{V^2}{2\pi\hbar^2/\sqrt{M_1M_2}KT}\right)^{N/2}$

The pressure is $p = \frac{1}{\beta}\frac{\partial \ln(Z)}{\partial V} = \frac{1}{\beta}\frac{\partial}{\partial V}(N\ln(V)) = \frac{1}{\beta}\frac{N}{V} = \frac{NKT}{V}$ before & after

The entropy is $S = K(\ln(Z) + \beta E) = K(\ln(Z) - \beta\frac{\partial \ln(Z)}{\partial\beta})$

Before: $\ln(Z_0) = N\ln(\frac{V}{2}) - \frac{N}{2}\ln(\beta) + \frac{N}{2}\ln\left(\frac{\sqrt{M_1M_2}}{2\pi\hbar^2}\right) - 2\ln(\frac{N}{2}!)$

$\Rightarrow S = K\left(N\ln(\frac{V}{2}) - \frac{N}{2}\ln(\beta) + \frac{N}{2}\ln\left(\frac{\sqrt{M_1M_2}}{2\pi\hbar^2}\right) - 2\ln(\frac{N}{2}!) + \frac{N}{2}\right)$

and $S' = K\left(N\ln(V) - \frac{N}{2}\ln(\beta) + \frac{N}{2}\ln\left(\frac{\sqrt{M_1M_2}}{2\pi\hbar^2}\right) - 2\ln(\frac{N}{2}!) + \frac{N}{2}\right)$

b. $\Delta S = KN(\ln(V) - \ln(\frac{V}{2})) = KN\ln(2)$ so it is irreversible, but $\Delta Q \neq T\Delta S$ because a free expansion of a gas is not quasistatic. In fact, for an adiabatic free expansion, $Q=0$ and $W=0 \Rightarrow \Delta E = 0$ and for an ideal gas $E = \frac{3}{2}NKT$ so $\Delta T = 0$. Therefore the reservoir at temperature T never exchanges any heat because it is always at the same temperature.

c. Before: $Z_0(N) = \frac{1}{(\frac{N}{2}!)^2}\left(\frac{V^2/4}{2\pi\hbar^2/MKT}\right)^{N/2}$ After: $Z_0'(N) = \frac{1}{N!}\left(\frac{V}{\sqrt{2\pi\hbar^2/MKT}}\right)^N$

$\Delta S = K\Delta(\ln(Z)) = K[N\ln(V) - \ln(N!) - N\ln(\frac{V}{2}) + 2\ln(\frac{N}{2}!)]$

If N is large, $\Delta S = K[N\ln(2) - N\ln(N) + \cancel{N} + 2(\frac{N}{2}\ln(\frac{N}{2}) - \cancel{\frac{N}{2}})]$

$= K[N\ln(2) - N\ln(N) + N\ln(N) - N\ln(2)] = 0$

So it is reversible and $\Delta Q = T\Delta S = 0$. The difference in entropy is due to the decrease in entropy due to indistinguishability.