Notes on Ideal Gas	**Max Zimet**
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First, Stirling's approximation: (logarithms are to base e)

$$\log(N!) = \sum_{n=1}^{N} \log n \approx \int_0^N \log n \, dn = n \log n - n|_0^N = N \log N - N, \tag{1}$$

for large N. (Note:

$$\lim_{n\to 0} n \log n = \lim_{n\to 0} \frac{\log n}{1/n} = \lim_{n\to 0} \frac{1/n}{-1/n^2} = \lim_{n\to 0}(-n) = 0,$$

using L'Hopital's Rule). Exponentiating both sides of (1) gives

$$N! \approx \left(\frac{N}{e}\right)^N. \tag{2}$$

Next, we have from the other set of notes that

$$dE = TdS - PdV.$$

Rearranging, we find that

$$dS = \frac{1}{T}dE + \frac{P}{T}dV,$$

or that

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E, \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V. \tag{3}$$

Now, we calculate Ω, so as to get $S = k_B \log \Omega$:

$$\Omega = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_0^L\int_0^L\cdots\int_0^L \frac{1}{h^{3N}}\, dx_1\, dy_1\, dz_1\, dx_2\, \ldots\, dz_N\, dp_{x,1}\, dp_{y,1}\, dp_{z,1}\, dp_{x,2}\, \ldots\, dp_{z,N}, \tag{4}$$

where the integral is subject to the constraint that

$$E = \frac{p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \ldots + p_{z,N}^2}{2M}. \tag{5}$$

(Recall that the volume element occupied by a microstate in phase space is h^{3N}, by the Heisenberg uncertainty principle, so that we divide by this to count the number of microstates). However, since each microstate occupies h^{3N} volume of phase space, this implies that the above constraint is incorrect, since we need to include fuzziness in the microstate's location in phase space, as specified by the Heisenberg uncertainty principle. The correct constraint is

$$E \leq \frac{p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \ldots + p_{z,N}^2}{2M} \leq E + \Delta,$$

where Δ is small.

The momentum integrals are just the volume of a spherical shell in $3N-$dimensional space, where the inner radius is $\sqrt{2mE}$ and the outer radius is $\sqrt{2m(E+\Delta)}$. The volume of the sphere of radius $R=\sqrt{2mE}$ in $3N$ dimensions is

$$\frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}R^{3N} = \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}(2mE)^{3N/2} \approx \left(\frac{4\pi emE}{3N}\right)^{3N/2},$$

where we have used Stirling's approximation. To get the volume of the shell, we differentiate this with respect to E, and multiply by Δ:

$$\Omega = \frac{3N}{2}\frac{\Delta}{E}V^N\frac{1}{h^{3N}}\left(\frac{4\pi emE}{3N}\right)^{3N/2}. \tag{6}$$

This is close, but not completely correct. In fact, this is the classical result (except for the h, which we got from the Heisenberg uncertainty principle. Classically (i.e., pre-quantum mechanics), people just ignored the fact that their Ω had the wrong units and really should have been infinite). However, it gives the wrong physics (for example, it makes S not extensive). The problem is that it treats each molecule as unique, when they are really identical. (Quantum mechanically, identical particles are actually indistinguishable, since there is no notion of a history or trajectory to differentiate them, as there is classically). So, we have over-counted the multiplicity by a factor of $N!$, the number of ways of re-arranging the molecules while getting the same microstate. So,

$$\Omega = \frac{3N}{2}\frac{\Delta}{E}V^N\frac{1}{N!h^{3N}}\left(\frac{4\pi emE}{3N}\right)^{3N/2} \approx \frac{3N}{2}\frac{\Delta}{E}\left(\frac{Ve}{N}\right)^N\frac{1}{h^{3N}}\left(\frac{4\pi emE}{3N}\right)^{3N/2}, \tag{7}$$

where I have used Stirling's approximation again.

We then calculate

$$S = k_B\log\Omega = k_B\left[\log\left(\frac{3N\Delta e^N(4\pi em)^{3N/2}}{2N^Nh^{3N}(3N)^{3N/2}}\right) + \frac{3N}{2}\log E - \log E + N\log V\right]. \tag{8}$$

Finally,

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E = k_B\frac{N}{V}, \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = k_B\left[\frac{3N}{2E} - \frac{1}{E}\right] \approx \frac{3Nk_B}{2E}, \tag{9}$$

since $N \gg 1$, giving the equations describing an ideal gas. Lastly, we re-write S to make it clear that it is extensive:

$$S = k_BN\left[\log\frac{V}{N} + \frac{3}{2}\log\frac{E}{N} + \frac{5}{2} + \frac{3}{2}\log\left(\frac{4m\pi}{3h^2}\right)\right]$$

(we have neglected tiny terms not proportional to N). Then, S is extensive. (Halving N, V, and E halves S).