Entropy

We have demonstrated that for a sufficiently slow process

$$\delta Q = T\,\delta\underbrace{\left(\frac{E}{T} + \ln Z\right)}_{\text{This is some function of state}}$$

Call it

$$S = \frac{E}{T} + \ln Z + \text{const}$$

S – entropy

$$T\,dS = E + P\,dV$$

We may rewrite the definitions of pressure and temperature using entropy

$$\boxed{P = -\left(\frac{\partial E}{\partial V}\right)_S \,, \quad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V}$$

Let's consider a closed cycle of changing the state of the system,

$$\oint dE = 0$$

Similarly

$$0 = \oint dS = \oint \frac{\delta Q}{T}$$

Because S is a function of state, we may measure it from whatever lavue we like, so const $\longrightarrow 0$

$\sigma = \frac{E}{T} + \ln Z$

Assume, only the most probable state contributes to entropy

$$Z = \sum_i e^{-\frac{\varepsilon_i}{T}} \approx \Omega(E)\, e^{-\frac{E}{T}}$$

Then $e^S = \Omega(E)$ and

$$S = \ln \Omega(E) = -\ln w_i$$

(Landau - Lifshitz : $S = -\langle \ln w_i \rangle$)