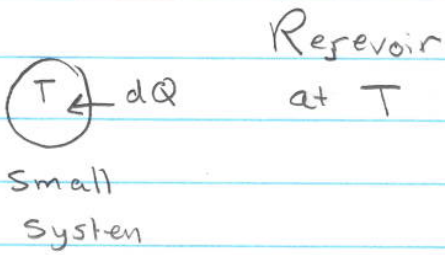
The First Law Revisited

$$dU = \text{đ}Q + \text{đ}W$$

- Now in an equilibrium process $\text{đ}W = -p\,dV$.
  We have argued that $dS_{\text{system}} = \dfrac{\text{đ}Q_{rev}}{T}$



- So

$$\boxed{dU = T\,dS - p\,dV}$$

- Now dU is an exact differential as is dS and dV, so we have

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

S-fixed
no heat flows in

So

$$\boxed{\begin{aligned} T &= \left(\frac{\partial U}{\partial S}\right)_V \\ p &= -\left(\frac{\partial U}{\partial V}\right)_S \end{aligned}}$$

$\Longrightarrow$ i.e. $dU_V = \text{đ}Q + \cancel{\text{đ}W}^{\,0} = T\,dS$

$\Longrightarrow$ i.e. $dU_S = \cancel{\text{đ}Q}^{\,0} - p\,dV$

- We can invert this: expressing $S(U,V)$ instead of $U(S,V)$

$$dU = T\,dS - p\,dV$$

or

$$\boxed{dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV}$$

So since

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

We have

$$\boxed{\left(\frac{\partial S}{\partial U}\right)_V \equiv \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{p}{T}}$$

Mechanical Equilibrium

- Consider two systems sharing the volume now, with no heat transfer allowed: E_1, E_2 fixed.

E_1	E_2
V_1	V_2

$$V_1 + V_2 = V$$

← we expect the two systems will equilibrate when $p_1 = p_2$

- As before the system will evolve to maximize the entropy (or probality)

$$S_{TOT} = S(V_1) + S_2(V_2)$$

- There is no heat transfer so E_1 and E_2 are fixed

$$\frac{dS_{TOT}}{dt} = \left(\frac{\partial S_1}{\partial V_1} \frac{dV_1}{dt} + \frac{\partial S}{\partial V_2} \frac{dV_2}{dt} \right) \geq 0$$

$$= \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right) \frac{dV_1}{dt} \geq 0$$

The volume V_1 will change until $\partial S_1 / \partial V_1 = \partial S_2 / \partial V_2$. Thus it is natural to define the pressure as

$$\boxed{\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_E}$$

see below for why temperature is there;

- This follows also from the first law:

$$dU \equiv đQ + đW \implies \frac{đQ}{T} = \frac{đU}{T} - \frac{đW}{T}$$

- So in a reversible process, $đW = -p\,dV$, $\frac{đQ}{T} = dS$, we have

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV$$

- We have for two subsystems, $\Delta S_{TOT} = \Delta S_1 + \Delta S_2$

$$\boxed{\Delta S_{TOT} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)\Delta V_1}$$

$U_1 + U_2 = \text{const}$

$V_1 + V_2 = \text{const}$

☆ The system will evolve so that $\Delta S > 0$. The volume V_1 will change until the pressure and temperature equilibrate

Entropy as Mother of All Things

- Consider the entropy of the ideal gas

$$\frac{S}{k_B} = N \ln V + \frac{3N}{2} \ln E + \text{const}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E = \frac{Nk}{V}$$

and

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3}{2}\frac{N k_B}{E}$$

So we see

$$\boxed{p = \frac{N k_B T}{V}} \quad \text{and} \quad \boxed{E = \frac{3}{2} N k_B T}$$

★ Thus by calculating the entropy of the ideal gas we have proved both the mono-atomic ideal gas EOS, $p = NkT/V$, and the energy of the system, $E = \frac{3}{2}NkT$.