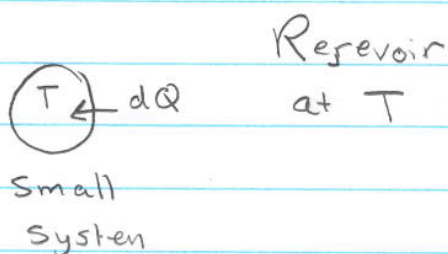


The First Law Revisited

$$dU = \delta Q + \delta W$$

- Now in an equilibrium process $\delta W = -p dV$.

We have argued that $dS = \frac{\delta Q_{\text{rev}}}{T}$



- So

$$dU = T dS - p dV$$

- 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

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V} \Rightarrow \text{i.e. } dU_V = \cancel{\delta Q} + \delta W = T dS$$

$$\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S} \Rightarrow \text{i.e. } dU_S = \cancel{\delta Q} - p dV$$

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

$$dU = T dS - p dV$$

or

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

So since

$$dS = \left(\frac{\partial S}{\partial u} \right)_v du + \left(\frac{\partial S}{\partial v} \right)_u dv$$

We have

$$\left(\frac{\partial S}{\partial u} \right)_v = \frac{1}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial v} \right)_u = \frac{p}{T}$$

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 probability)

$$S_{\text{TOT}} = S_1(V_1) + S_2(V_2)$$

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

$$\frac{dS_{\text{TOT}}}{dt} = \left(\frac{\partial S_1}{\partial V_1} \frac{dV_1}{dt} + \frac{\partial S_2}{\partial V_2} \frac{dV_2}{dt} \right) \geq 0$$

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

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

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

see below for why temperature is there:

- This follows also from the first law:

$$dU \equiv dQ + dW \Rightarrow \frac{dQ}{T} = \frac{dU}{T} - \frac{dW}{T}$$

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

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

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

$$\Delta S_{\text{TOT}} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \Delta U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) \Delta V_1, \quad \begin{aligned} U_1 + U_2 &= \text{const} \\ V_1 + V_2 &= \text{const} \end{aligned}$$

- ★ 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

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

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

and

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

So we see

$$p = \frac{Nk_B T}{V}$$

and

$$E = \frac{3}{2} Nk_B T$$

★ 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, $E = \frac{3}{2} NkT$.