The First Law Revisited: Mechanical Equilibrium

The energy satisfies

$$dU = đQ - đW_{out}$$

Now if the heat is added slowly to an equilibrated system and rethermalized $đQ = T\,dS = dQ_{rev}$

☆ $$\boxed{dU = T\,dS - p\,dV} \quad \text{or} \quad dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV$$

Now consider $U(S,V)$

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

Comparison gives

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V} \qquad \boxed{p = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial U}{\partial V}\right)_{adiab}}$$

we had this as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$$

no heat flows in $dU = -p\,dV$
S is constant when no heat flows in

We can work with $S(U,V)$ instead of $U(S,V)$
from ☆ we find after minor algebra:

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

Now consider $S(U, V)$

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

Comparison gives

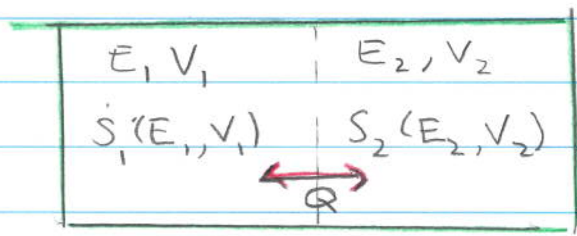
See next section!

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

We will derive these again in the next section.

Mechanical Equilibrium

- Consider two gasses sharing the energy and volume. If the volume of gas #1 increases there will be more configurations it can explore (its states are labelled by the positions and momenta of the particles). Thus the entropy is a funcition of energy and volume $S(E, V)$



$$E_1 + E_2 = E = \text{const}$$

$$V_1 + V_2 = V = \text{const}$$

- We expect the two gasses will equilibrate when they are at equal temperature and pressure

$$\boxed{S_{TOT} = S_1(E_1, V_1) + S_2(E_2, V_2)}$$

The entropy of the combinded system is a sum of the entropy of the two systems when partitioned into (E_1, E_2) and (V_1, V_2)

Then the entropy increases in time changing E_1 and V_1:

$$\frac{dS_{TOT}}{dt} = \left(\frac{\partial S_1}{\partial E_1}\frac{dE_1}{dt} + \frac{\partial S_2}{\partial E_2}\frac{dE_2}{dt}\right) + \left(\frac{\partial S_1}{\partial V_1}\frac{dV_1}{dt} + \frac{\partial S_2}{\partial V_2}\frac{dV_2}{dt}\right) > 0$$

Now $E_1 + E_2 = \text{const}$ so $\dot{E}_1 + \dot{E}_2 = 0$ and

Similarly

$$V_1 + V_2 = \text{const} \quad \text{so} \quad \dot{V}_1 + \dot{V}_2 = 0$$

So entropy increases as:

$$\frac{dS_{TOT}}{dt} = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) \frac{dE_1}{dt} + \left(\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} \right) \frac{dV_1}{dt} > 0$$

Now $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T}$ so

We have

$$\boxed{\frac{dS_{TOT}}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \frac{dV_1}{dt} > 0}$$

Thus the entropy will increase until

$$\frac{1}{T_1} = \frac{1}{T_2} \quad \text{and} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

i.e. until the temperatures and temperatures are equal.