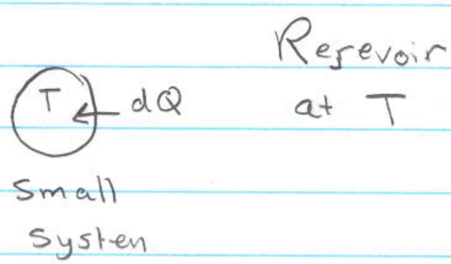
The First Law Revisited

$$dU = \bar{d}Q + \bar{d}W$$

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



- 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. $dU_V = \bar{d}Q + \cancelto{0}{\bar{d}W} = T\,dS$

$\Longrightarrow$ i.e. $dU_S = \cancelto{0}{\bar{d}Q} - p\,dV$

- 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

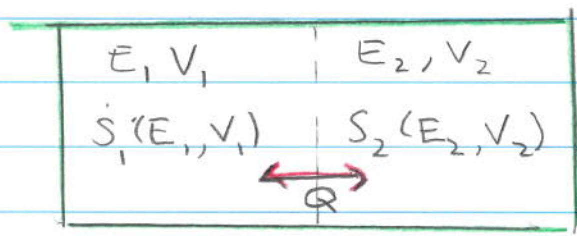
$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

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 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.