Entropy & Heat

Suppose V & N are constant, & $W=0$

$$dU = Q$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} \xrightarrow[\text{const}]{V,N} dS = \frac{1}{T}\,dU = \frac{Q}{T}$$

or $Q = T\,dS$

Generally, $Q = C_V\,dT$

$$\therefore\ dS = C_V \frac{dT}{T}$$

For non-infinitesimal changes

$$\Delta S = S_f - S_i = \int_{S_i}^{S_f} dS = \int_{T_i}^{T_f} C_V \frac{dT}{T}$$

if C_V is constant,

$$\Delta S = C_V\left[\ln T\right]_{T_i}^{T_f} = C_V \ln \frac{T_f}{T_i}$$

e.g. Heat 1 kg of water from $20^\circ C \to 100^\circ C$
$293K \to 373K$

$c_v = 4179\ J/k/kg$ constant

$C_V = 4179\ J/k$

$$\Delta S = 4179 \ln \frac{373}{293} = 1008\ J/k$$

$$S = k \ln \Omega \to \Omega = e^{S/k}$$

$$\Omega_f = \Omega_i e^{\Delta S/k} = \Omega_i e^{1008\,J/k/k} = \Omega_i e^{7.3\times 10^{25}}$$

To define S instead of ΔS, we need a baseline

At $T = 0$, $\Omega = 1$ (no motion. state is fixed)

$\therefore$ $S = 0$ at $T = 0$.

Third Law of Thermodynamics

$$\Delta S = S(T) - S(0) = \int_0^T \frac{C_V}{T} dT$$

$$S(T) = \cancel{S(0)}^{\,0} + \int_0^T \frac{C_V}{T} dT$$

if C_V constant, $S(T) = C_V \ln \frac{T}{0} = \infty$

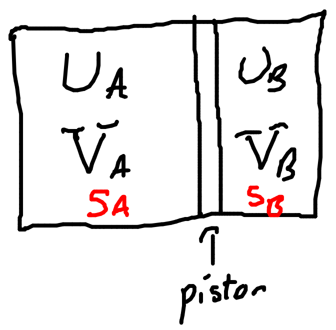
$\therefore$ C_V cannot be constant but must go to zero as $T \to 0$

e.g. equipartition theorem $C_V = N \frac{f}{2} k$

as $T \to 0$, $f \to 0$: "freezing out"

f: # d.o.f.

Mechanical Equilibrium



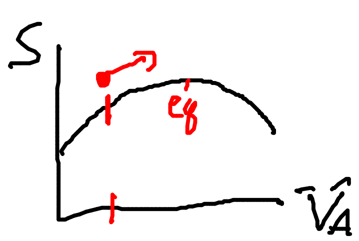
$U_A + U_B = U$
$V_A + V_B = V$ } fixed
$S_A + S_B = S$

Piston will stop moving (equilibrium) when

- pressures are equal
- entropy $S(V_A)$ is maximized

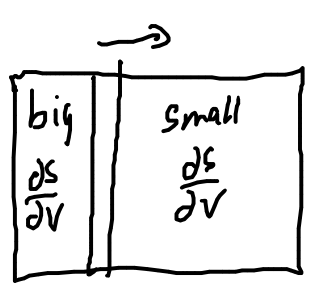
- $\dfrac{\partial S}{\partial V_A} = 0 = \dfrac{\partial S_A}{\partial V_A} - \dfrac{\partial S_B}{\partial V_B}$

- $\left(\dfrac{\partial S}{\partial V}\right)_{U,N}$ is same on both sides



V_A will increase

$\dfrac{\partial S}{\partial V_A} > 0 \rightarrow \dfrac{\partial S_A}{\partial V_A} > \dfrac{\partial S_B}{\partial V_B}$



Just like pressure

$\dfrac{\partial S}{\partial V} \propto P$

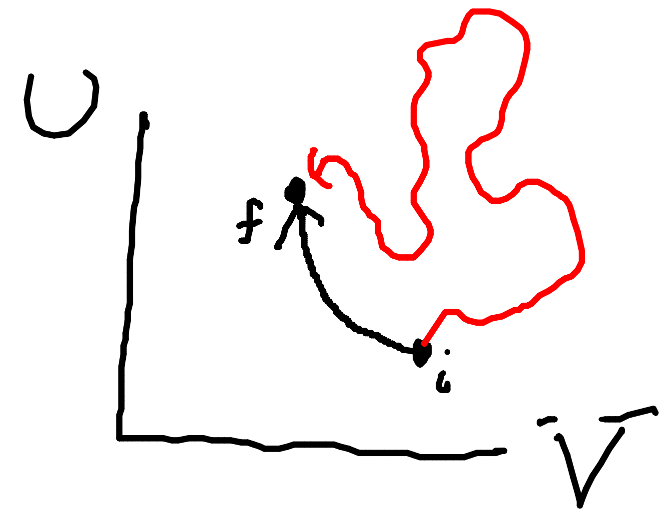
Units: $\left[\dfrac{\partial S}{\partial V}\right] = \dfrac{J/K}{m^3} = \dfrac{Nm}{m^3 K} = \dfrac{N}{m^2 K} = \dfrac{Pa}{K}$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}}$$

e.g. ideal gas $\quad S = Nk \ln V + U, N \text{ stuff}$

$\dfrac{\partial S}{\partial V} = \dfrac{Nk}{V} = \dfrac{P}{T} \rightarrow PV = NkT$ ideal gas law

What if U & V both change?



U & V are state variables

depend on current state of system,

but not on how it got there.

P, V, N, T, U all state variables

Q & W are not

Entropy is a state variable too.

To calculate $\Delta S = S_f - S_i$ I can use any path