Enthropy — how disordered are you?

New state variable : enthropy S
(other state variables: P, V, T, n, E_{int})

On the macroscopic level we can only define the change of enthropy

$$dS = \frac{dQ}{T} \qquad \Delta S_{12} = \int_{T_1\,(\text{state}1)}^{T_2\,(\text{state}2)} \frac{dQ}{T}$$

Adiabatic process: $dQ = 0 \Rightarrow dS = 0 \quad S = \text{const}$
another name: isentropic process

Isothermal process: $T = \text{const} \qquad dS = \frac{dQ}{T} \Rightarrow \Delta S_{12} = \frac{1}{T}\int_{\text{state}1}^{\text{state}2} dQ = \frac{x(}{T}$

This expression is valid for phase transitions as well: $T = \text{const} \quad Q = mL \Rightarrow \Delta S = mL/T$

Example: When $m = 0.1\,kg$ of ice melts, how much the enthropy increases?

$L_{fusion} = 3.34 \cdot 10^5\ J/kg \qquad T = 0^\circ C = 273K$

$$\Delta S_{melting} = \frac{0.1kg \cdot 3.34 \cdot 10^5\ J/kg}{273K} = 122\ J/K$$

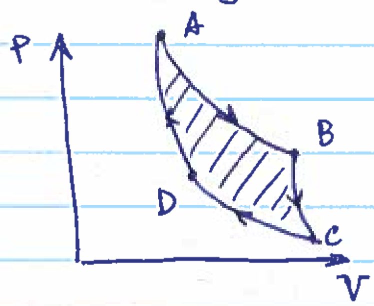
Isochoric process: $Q = nC_v T \Rightarrow dQ = nC_v\,dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_v\,dT}{T} = nC_v \ln T_2/T_1$$

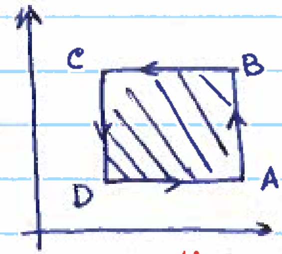
Isobaric process: $Q = nC_p T \Rightarrow dQ = nC_p\,dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_p\,dT}{T} = nC_p \ln T_2/T_1$$

Carno cycle in S-T coordinates



Area of the cycle in P-V → total work W



$dS = \frac{dQ}{T}$

$dQ = TdS$

Area of the cycle in S-T → total heat Q

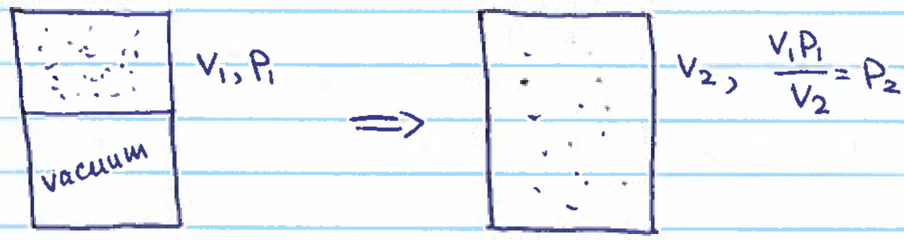
Since entropy is a state variable, ideal closed cycle is reversible: it can be repeated in the opposite direction, with no other change anywhere else in the universe.
Like unicorns, they don't exist

In reversible processes the system always stays in equilibrium (the whole system is in the same state as any of its part and can be defined by same set of state variables)
Thus such processes must be slow
- isothermal compression / expansion
- slow adiabatic ——— " ———

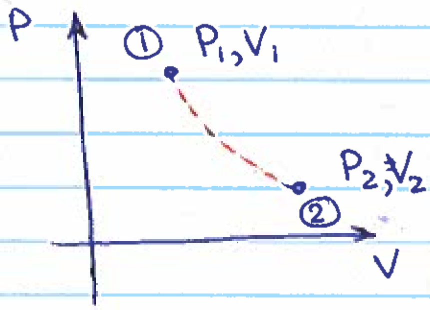
What makes a process irreversible?
- friction (converts useful energy into waste)
- open system from which energy escapes and cannot be recaptured
- irreversible ~~mixing~~ processes, like mixing of different substance

Example: free gas expansion $V_1 \rightarrow V_2$

$Q = 0$, T = constant so $\Delta E_{int} = 0$ $\quad$ $\Delta S = 0$? no! irreverisble process!



need a different way to calculate



What reversible process gets us from ① to ② ?

Isothermal! $\Delta Q = W = nRT \ln \frac{V_2}{V_1}$

$$\Delta S = \frac{\Delta Q}{T} = nR \ln \frac{V_2}{V_1} > 0$$

Since the initial and final states are the same for irreversible process, there will be the same change in enthropy $\Delta S = nR \ln V_2/V_1 > 0$

For an ideal reversible process the enthropy of a closed system does not change

ΔS (system + environment) $= 0$

For any natural process $\Delta S > 0$

Another formulation of the 2nd law of thermodynamics:

The enthropy change of an isolated system can never be negative

or

The enthropy of the Universe (as an isolated system) will always increase over time.

The increase of enthropy sets the arrow of time.