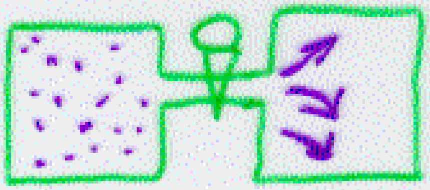
Entropy and the 2nd Law of T.D.

One-way (irreversible) processes

e.g. ① Free expansion of a gas:



- energy conserved
- both adiabatic ($Q=0$) and isothermal ($\Delta T = 0$)

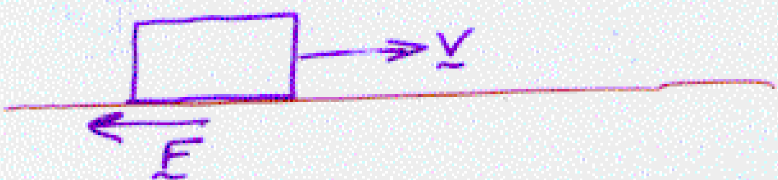
Gas flows from high $p \rightarrow$ low p, never the other way.

② Similarly, Heat flows hot $\xrightarrow{Q}$ cold

never: cold $\rightarrow$ hot ×

③ Can convert Work $\xrightarrow{100\%}$ heat Q

e.g. friction slows moving object $\rightarrow$ heats object + surface



(Never: heat object $\rightarrow$ starts to move!)

Energy conserved either forwards or backwards in all 3 cases – so what's going on ???

A: Some other property of (initial, final) state determines an "arrow of time" .....

Definition of Entropy Change between states

Define : $\boxed{\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}}$

where Q = heat input into system.

Why? It turns out that entropy S depends only on the state of a system, not the path taken (like W or Q).

Entropy S is a "state property", like E_{int} or T.

"Proof" for an ideal gas when $V_i \Rightarrow V_f$, $T_i \Rightarrow T_f$:

$$\Delta S = \int \frac{dQ}{T} = \int \frac{dE}{T} + \int \frac{dW}{T} \quad \text{(1st law)}$$

$dE = nC_v dT$ $\quad$ $dW = PdV$ $\quad$ $T = \frac{PV}{nR}$

$$\Rightarrow \Delta S = C_v \int \frac{dT}{T} + nR \int \frac{dV}{V}$$

i.e. $\boxed{\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)}$: ideal gas

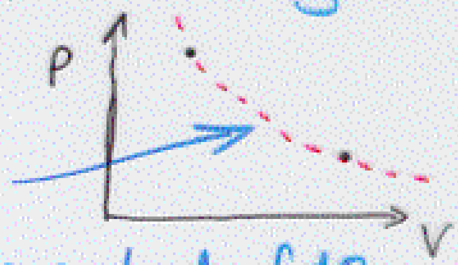
Note: ΔS depends only on (initial, final) values of T, V as required.

$\Rightarrow$ easy to calculate even for irreversible processes

For an ideal gas, we have $\Delta S = \int \frac{dQ}{T}$

i.e. $$\Delta S = \overbrace{n c_v \ln\left(\frac{T_f}{T_i}\right)}^{\text{internal energy}} + \overbrace{nR\ln\left(\frac{V_f}{V_i}\right)}^{\text{work}} \quad (*)$$

Note: Although derivation assumes that P, V, T vary smoothly, ΔS is same for any process connecting states – even a free expansion!



connect states with a reversible isothermal change to do $\int \frac{dQ}{T}$

Isothermal or Free Expansion : $T_f = T_i =$ constant

So $$\Delta S = \int \frac{dQ}{T} = \frac{1}{T}\int dQ = \frac{Q}{T} = nR\ln\left(\frac{V_f}{V_i}\right) \text{ from } (*)$$

Constant-vol process : $V_f = V_i$ so $\Delta S = n c_v \ln\left(\frac{T_f}{T_i}\right)$

Isobaric process : $\frac{V_f}{V_i} = \frac{T_f}{T_i}$ so $\Delta S = n c_v \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{T_f}{T_i}\right)$

i.e. $$\Delta S = n(c_v + R)\ln\left(\frac{T_f}{T_i}\right) = n c_p \ln\left(\frac{T_f}{T_i}\right)$$

Adiabatic process : $dQ = 0$ so $\Delta S = \int \frac{dQ}{T} = 0$ (phew!)

Examples:

1 mole of monatomic gas doubles its volume:

1. Adiabatic $\Delta S = 0$

2. Isobaric $\Delta S = n(c_v + R)\ln\left(\frac{T_f}{T_i}\right)$

   Monatomic gas has $c_v = \frac{3}{2}R$

   $\Rightarrow \Delta S = n \cdot 2.5 R \ln 2 = 14.4\ \mathrm{J/K}$

3. Isothermal $\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) = nR\ln 2$
   $= 5.76\ \mathrm{J/K}$

4. Free expansion – $\Delta T = 0$ so same as isothermal.

Note: If we run processes 1, 2, 3 backwards then $\Delta S \leq 0$, looks OK

<u>But</u> cannot run 4 backwards – irreversible

∴ 2nd law of TD part A:

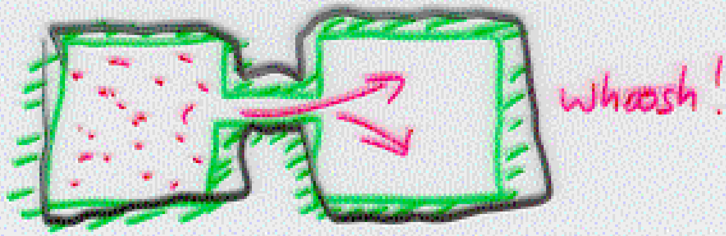
$\Rightarrow$ "In a closed system, entropy always increases for irreversible processes."

i.e. ΔS defines direction of videotape for sending to E.T.

– play tape such that $\Delta S > 0$

Reversible + Irreversible Processes

For free expansion :



gas container is a "closed system" and $\Delta S > 0$

But for reversible, isothermal process :

Heat Q enters / leaves from reservoir to keep T constant

So although gas has $\Delta S = \frac{+Q}{T} = nR\ln\left(\frac{V_f}{V_i}\right) > 0$

reservoir has $\Delta S_{res} = \frac{-Q}{T}$

$\therefore$ for closed system of reservoir + gas , $\Delta S_{tot} = 0$

> $\Rightarrow$ 2nd law of TD , part B :
> "In a closed system, entropy does not change for reversible processes

i.e. For reversible process, can play videotape in either direction

$\Delta S = 0$ does not define arrow of time

Summary: 2nd Law of Thermodynamics

$$\boxed{\text{For a closed system: } \quad \Delta S = \int \frac{dQ}{T} \geqslant 0}$$

$\Delta S > 0$ for irreversible process

$= 0$ " reversible

< 0 NEVER! - So if you find $\Delta S < 0$, system must not be closed, and $\Delta S > 0$ somewhere else.

"Irreversible entropic processes in brain may define the "arrow of time" in our consciousness."

— tell this to Hare Krishnas, then run!

e.g. Play video backwards of:

- air hockey game : reversible, $\Delta S = 0$, looks OK
- Die Hard II : explosions irreversible, so looks "wrong" in reverse

Read: A Brief History of Time by Stephen Hawking

- excellent discussion of time's arrow.