

For the case of pure heating, $dE = dQ$

$$dS = \frac{dQ}{T} \quad (\text{quasistatic})$$

$\Rightarrow \Delta S = 0$ in quasistatic, adiabatic process

Note: Basic rules outlined thus far can be used to understand that there is a maximum efficiency for any engine (Carnot efficiency) which can be calculated irrespective of details

More definitions: $\frac{P}{T} \equiv \left(\frac{\partial S}{\partial V} \right)_{E, N}$ thermodynamic pressure, $\frac{\mu}{T} \equiv$

Measuring entropy

How do we measure entropy changes in a real system? There is no entropy meter...

$\Rightarrow C, T$ easy to measure

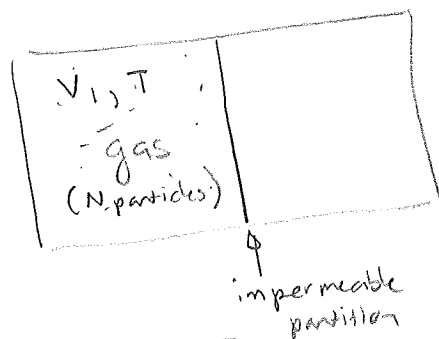
\Rightarrow use a quasistatic process to change the temperature of a system from T_1 to T_2

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} C(T) \frac{dT}{T}$$

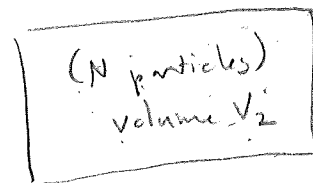
Ex: For a solid, $C \approx \text{const}$ with temperature and $C_v \approx C_p$

$$\Delta S = C \int_{T_1}^{T_2} \frac{dT}{T} = C \log(T_2/T_1)$$

Ex: Free expansion of an ideal gas



\Rightarrow



What is ΔS ?

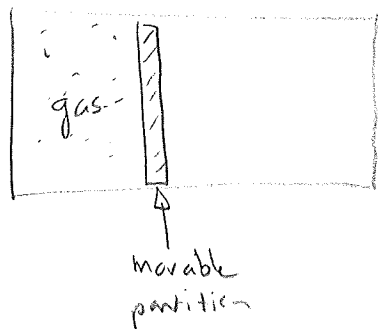
no energy enters / leaves \Rightarrow internal energy of gas doesn't change

$$\Delta S = \frac{Q}{T} = 0 \quad ???$$

This conclusion is incorrect as this is not a quasistatic process $\Delta S = \cancel{\frac{Q}{T}}$

However, entropy is a state function so we can consider any process $1 \rightarrow 2$

\Rightarrow should be quasistatic so we can use rules of thermodynamics



gas does work W to increase volume ΔV

$$W = -P\Delta V$$

recall: $\Delta E = 0 \Rightarrow Q = -W$

Then, $\Delta S = \frac{Q}{T} = -\frac{W}{T}$

$$= \int_{V_1}^{V_2} \frac{P dV}{T}$$

$$= \int_{V_1}^{V_2} \frac{NkT dV}{T}$$

$$\boxed{\Delta S = Nk \log(V_2/V_1)}$$

$\Delta S > 0$ as we expect!

Note: thermodynamics is confusing

\Rightarrow we only care about equilibrium states,
there is no dynamics!

\Rightarrow we often consider processes that did not
actually happen (only initial / final states matter)

Fundamental thermodynamic relation

recall: $\Delta E = W + Q$

for an infinitesimal, quasistatic change

$$dW = -P dV, \quad dQ = T dS$$

$$\Rightarrow dE = T dS - P dV$$

if we additionally allow particle number to vary

$$\boxed{dE = T dS - P dV + \mu dN}$$

FUNDAMENTAL THERMO.
RELATION
MEMORIZE!

↑
chemical
potential

- mathematical statement that combines 1st & 2nd laws
- starting point for deriving many useful relations!

recall: for any function $\theta(x, y, z)$ we can write its exact differential as

$$d\theta = \left(\frac{\partial \theta}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \theta}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \theta}{\partial z}\right)_{x,y} dz$$

Thus, if we consider the natural variables for E as S, V, N

$$dE = \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial N}\right)_{V,S} dN$$

comparing with fundamental relation

$$dE = T dS - P dV + \mu dN$$

$$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_{V,N} = T$$

$$\left(\frac{\partial E}{\partial V}\right)_{S,N} = -P$$

$$\left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu$$

The entropy can be treated in a similar manner by rearranging the above:

$$T dS = dE + P dV - \mu dN$$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

but we can also say:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,E} dN$$

Now we see where definitions come from!

- E, V, N are "natural variables" for S
- S, V, N are natural variables for E
- both E and S are thermodynamic potentials as their partial derivatives yield eqns of state

Third law of thermodynamics

We have seen that the various thermodynamic relations can be used to calculate changes in entropy.

e.g. free expansion, $\Delta S = \frac{Q}{T} = \frac{-W}{T} = Nk \log(V_1/V_2)$

third law \Rightarrow absolute value of S

$$\boxed{\lim_{T \rightarrow 0} S = 0} \quad \text{3rd law}$$

\rightarrow we will state this more precisely when we get to stat mech

Consequence : heat capacities $\rightarrow 0$ as $T \rightarrow 0$

- consider change at constant volume

$$S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT \quad (\text{by definition})$$

$T_1 \rightarrow 0 \Rightarrow$ 3rd law says integral finite

$\Rightarrow C_V(T) \rightarrow 0$ as $T \rightarrow 0$

(can make similar argument for C_p)

- low temperature behavior of C_V, C_p independent of details of system!
- established experimentally near turn of 20th century
- note : ideal gas $C_V = \frac{3}{2} Nk$
 $C_p = \frac{5}{2} Nk$ } must break down at low T !