Now $\Delta V = -A\delta$ where A is the area of the piston ($V = AL$). So

$$\Delta S = \frac{3}{2} k \frac{f\delta}{E/N} - \frac{NkA\delta}{AL}.$$

Now $\frac{E}{N} = \frac{3}{2} kT$, so

$$\Delta S = \frac{f\delta}{T} - \frac{Nk\delta}{L} = \frac{\delta}{T}\left(f - \frac{NkT}{L}\right).$$

The entropy increases until equilibrium is reached at $L = L_0$ where $\Delta S = 0$

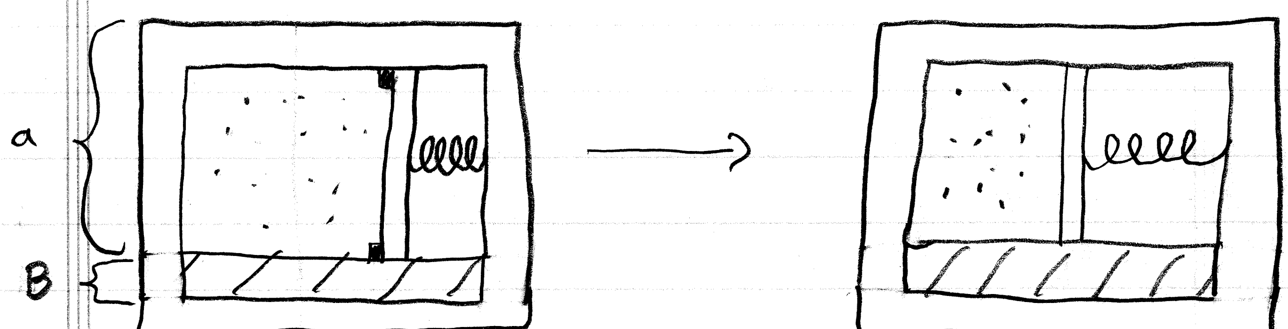
$$0 = \Delta S = \frac{\delta}{T}\left(f - \frac{NkT}{L_0}\right).$$

So $f = \frac{NkT}{L_0}$ and $L_0 = \frac{NkT}{f}$.

Setting $f = pA$ where p is the pressure, we get $pL_0A = pV = NkT$ which is the ideal-gas law.

When a constraint is removed, the number Ω of microstates rises, and so does the entropy $S = k \ln \Omega$.

This "irreversibility" is due to the choice of a constrained initial state, e.g., all molecules on one side of the box, and not to a breakdown of time-reversal symmetry.



System a (gas & spring) can exchange heat with system B, which is a big slab of Iron whose temperature T_B remains nearly constant. B is a <u>thermal</u> <u>reservoir</u>.

We release the brakes, and the spring compresses the gas whose temperature T_a initially rises but then subsides to $T_B = T$ as the combined system reaches equilibrium.

So $E_{gas} = \frac{3}{2}NkT$ does not change, but E_{spring} does change — it goes down. So

$$\Delta E_a = \Delta(E_{gas} + E_{spring}) = -f\delta.$$

So

$\Delta S_a = \Delta S_{gas} + \Delta S_{spring}$, we ignore ΔS_{spring}.

So $$\Delta S_a = \Delta S_{gas} = \Delta k \ln E_{gas}^{\frac{3N}{2}} V^N = \frac{Nk}{V}\Delta V$$

$\Delta V = -A\delta$, so

$$\Delta S_a = -\frac{NkA\delta}{AL} = -\frac{Nk\delta}{L}.$$

We must include system B. Now

$$T = \left(\frac{dS_B}{dE}\bigg|_V\right)^{-1} \quad \text{so} \quad \Delta S_B = \frac{\Delta E_B}{T} = -\frac{\Delta E_a}{T}.$$

Thus when $S = S_a + S_B$ is maximal

$$\Delta S = \Delta S_a + \Delta S_B$$

$$= -\frac{Nk\delta}{L} - \frac{(-f\delta)}{T}$$

$$= \frac{\delta}{T}\left(f - \frac{NkT}{L}\right)$$

which again gives $L_0 = \frac{NkT}{f}$ and

with $f = pA$

$$pV = NkT$$

which is the ideal-gas law. (that was $\boxed{6C}$)

So when we consider a small system "a" in thermal contact at fixed volume with a much larger thermal reservoir, the release of a constraint minimizes

$$F_a = E_a - TS_a.$$

Here T is the fixed temperature of the thermal reservoir. $F = E - TS$ is the <u>Helmholtz free energy</u>.

System "a" can do useful work until its free energy $F_a = E_a - TS_a$ slides to its minimum. Here

$$0 = \Delta S = \Delta S_a + \Delta S_B$$

$$= \Delta S_a - \frac{\Delta E_a}{T}$$

So

$$0 = -T\Delta S = \Delta F_a = \Delta E_a - T\Delta S_a.$$

Now replace the spring with a rod and push or pull on the piston.

Then

$$\frac{dF_a}{dL} = \frac{d(E_a - TS_a)}{dL} \qquad E_a \text{ is constant}$$

$$= -T\frac{dS_a}{dL} = -T\frac{d\,k \ln V^N}{dL} = -\frac{kNTA}{V}$$

So that

$$-\frac{dF_a}{dL} = \frac{kNT}{L} = f_a .$$

The force of the rod compressing the gas is called an entropic force.

The maximum amount of work system a can do is

$$\int_L^{L_m} f_a \, dL = -\int_L^{L_m} \frac{dF_a}{dL} dL = F(L) - F(L_m).$$

An abstract definition of pressure p is

$$p = T \left.\frac{dS}{dV}\right|_E , \qquad (6.15)$$

We also have

$$T = \left(\left.\frac{dS}{dE}\right|_V \right)^{-1} = \left(\frac{dS}{dQ}\right)^{-1}, \quad (6.9)'$$

$\boxed{6D}$ Ideal gas:

$$S = k \ln E^{\frac{3N}{2}} V^N$$

$$\left.\frac{dS}{dV}\right|_E = \frac{Nk}{V} = \frac{p}{T}$$

So we again get $pV = NkT$, which is the ideal-gas law.

The Gibbs free energy G is

$$G = E + pV - TS. \qquad (6.16)$$

If small system "a" is in thermal and mechanical contact with a huge system B of constant temperature T and constant pressure p, then when we release a constraint on a, new microstates will open until

$$G_a = E_a + pV_a - TS_a$$

is minimized.

The Skinny on Free Energy

First, we define the temperature T as

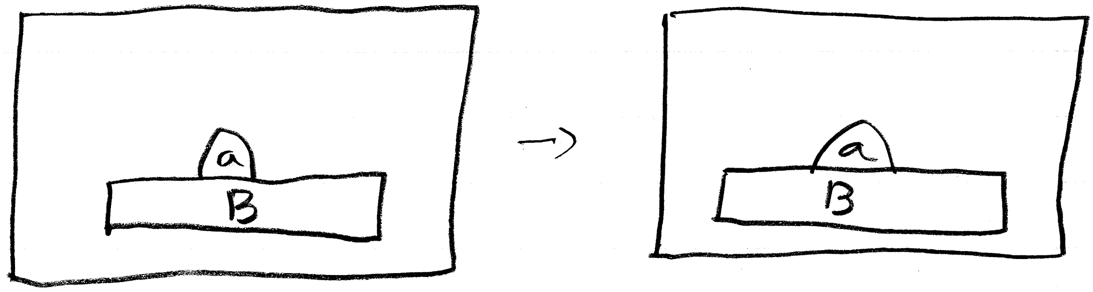
$$T = \left(\frac{\partial S}{\partial E}\bigg|_V \right)^{-1} = \left(\frac{\partial S}{\partial Q} \right)^{-1} \qquad (6.9)$$

and the pressure p as

$$p = T \, \frac{\partial S}{\partial V}\bigg|_E \, . \qquad (6.15)$$

Second, following Helmholtz, we consider a small system "a" in thermal contact at fixed volume V with a huge thermal reservoir "B." The total entropy $S = S_a + S_B = k \ln \Omega$ will increase to its maximum if we relax some constraints

$$\Delta S = \Delta S_a + \Delta S_B .$$



Heat flows out of a or into a.

$$\Delta E_a = -\Delta E_B.$$

$$\Delta S_B = \left.\frac{\partial S_B}{\partial E_B}\right|_V \Delta E_B = \frac{1}{T}\Delta E_B = -\frac{\Delta E_a}{T}.$$

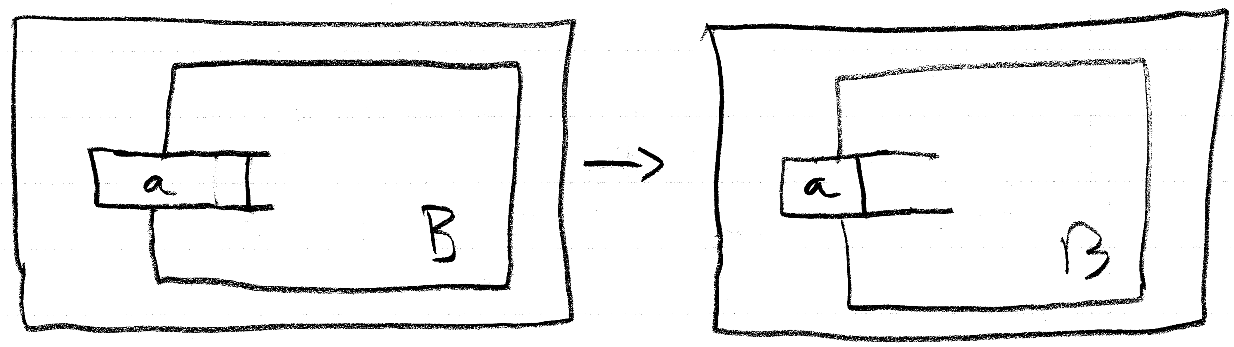
At equilibrium, $0 = \Delta S$

$$0 = \Delta S = \Delta S_a - \frac{\Delta E_a}{T} \quad \text{or}$$

$$0 = \Delta\left(-\frac{F_a}{T}\right) = \Delta S_a - \frac{\Delta E_a}{T}$$

So $F_a = E_a - TS_a$ is a minimum at equilibrium.

Third, following Gibbs, consider a small system "a" in thermal and mechanical contact with a huge system "B" whose pressure p and temperature T remain constant.



Release constraints and watch the number Ω of microstates grow until $S = S_a + S_B$ is maximal.

At its maximum

$$0 = \Delta S = \Delta S_a + \Delta S_B .$$

For small changes of E_B and V_B

$$\frac{1}{T} = \frac{1}{T_B} = \left.\frac{\partial S_B}{\partial E_B}\right|_{V_B} \quad \text{and} \quad \frac{p}{T} = \left.\frac{\partial S_B}{\partial V_B}\right|_{E} .$$

So

$$0 = \Delta S = \Delta S_a + \frac{\partial S_B}{\partial E_B}\Delta E_B + \frac{\partial S_B}{\partial V_B}\Delta V_B$$

or

$$0 = \Delta S_a + \frac{1}{T}\Delta E_B + \frac{P}{T}\Delta V_B$$

$$0 = \Delta S_a - \frac{\Delta E_a}{T} - \frac{P}{T}\Delta V_a .$$

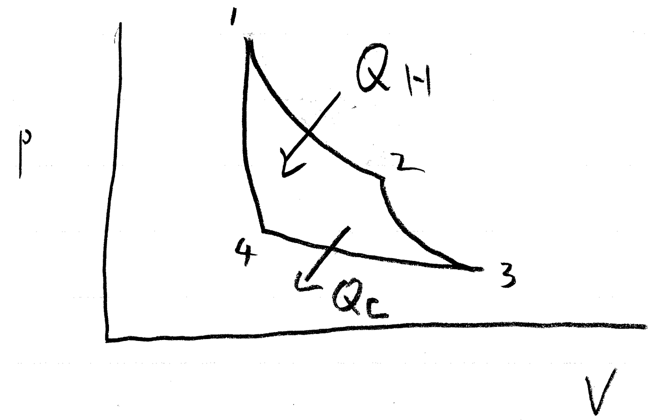
So when S is maximal, the Gibbs free energy

$$G_a = E_a + pV_a - TS_a$$

is minimal because

$$0 = \Delta S_a = \Delta\left(-\frac{G_a}{T}\right).$$

The Carnot cycle



$1 \to 2$ is isothermal at T_H, $Q_H = T_H \Delta S_{12}$

$2 \to 3$ is addabatic, T_H drops to T_C

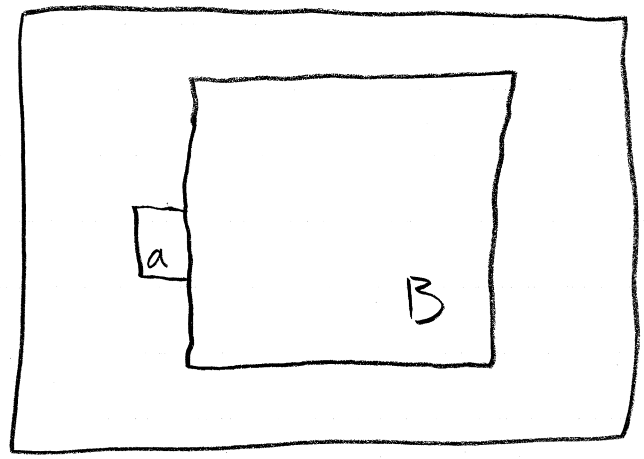
$3 \to 4$ is isothermal at T_C, $Q_C = T_C |\Delta S_{34}|$

$4 \to 1$ is adiabatic, T_C rises to T_H

Since $\Delta S_{12} = |\Delta S_{34}|$, the efficiency is

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}.$$

Suppose $T_H = 600°C \approx 900K$, if global warming raises T_C from 300 to 303, then the efficiency of all such motors will drop by $\Delta e = -\frac{3}{900} \approx -\frac{1}{3}\%$.



$$E = E_a + E_B$$

We assume that all microstates of total energy E of the joint system $a + B$ are equally likely. Each has probability P_0. The number of microstates of the huge system B is $\Omega_B(E_B)$. Since $S_B(E_B) = k \ln \Omega_B(E_B)$, it follows that

$$\ln \Omega_B(E_B) = S_B(E_B)/k$$

or
$$\Omega_B(E_B) = e^{S_B(E_B)/k}.$$

So the probability of a being in a single microstate of energy E_a and $\mathcal{B}$ being in any of the $\Omega_{\mathcal{B}}(E_{\mathcal{B}})$ microstates of energy $E_{\mathcal{B}} = E - E_a$ is

$$P(E_a) = P_0\, \Omega_B(E_B) = P_0\, e^{S_B(E_B)/k}$$

$$= P_0\, e^{S_B(E - E_a)/k}$$

$$\cong P_0\, e^{S_B(E) - \frac{E_a}{k}\frac{dS_B(E)}{dE}},$$

But since

$$\frac{1}{T} = \left.\frac{\partial S_B}{\partial E}\right|_V,$$

we have

$$P(E_a) \cong P_0\, e^{S_B(E) - \frac{E_a}{kT}}$$

or

$$P(E_a) \cong \text{constant}\; e^{-\frac{E_a}{kT}}$$

which is the Boltzmann distribution.

If the tiny system a has only two states, then for some constant c

$$P_1 = c\, e^{-E_1/kT}$$

$$P_2 = c\, e^{-E_2/kT}$$

and $\quad P_1 + P_2 = 1. \quad$ So

$$\frac{P_1}{P_2} = e^{\Delta E/kT} \qquad \Delta E = E_2 - E_1$$

So

$$\frac{P_1}{P_2} + 1 = \frac{1}{P_2} = e^{\Delta E/kT} + 1$$

or

$$P_2 = \frac{1}{1 + e^{\Delta E/kT}}$$

and

$$P_1 = \frac{e^{\Delta E/kT}}{1 + e^{\Delta E/kT}} = \frac{1}{1 + e^{-\Delta E/kT}}.$$

At high T, $P_1 \approx P_2$. But if $E_2 \gg E_1 + kT$, then $P_2 \approx 0$ and $P_1 \approx 1$.

$\boxed{6F}$ Suppose

$$E_a(x,v) = \frac{1}{2} m v^2 + \frac{1}{2} c x^2.$$

Then

$$\langle E_a \rangle = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv \; E_a(x,v) \, P(x,v)$$

where

$$P(x,v) = N \, e^{-E_a(x,v)/kT}$$

and

$$N = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dv \; e^{-E_a(x,v)/kT}.$$

So

$$P(x,v) = \left(\sqrt{\frac{m}{2\pi kT}} \, e^{-\frac{mv^2}{2kT}} \right) \left(\sqrt{\frac{c}{2\pi kT}} \, e^{-\frac{cx^2}{2kT}} \right)$$

$$\equiv P(v) \quad P(x)$$

in which each factor $P(v)$ & $P(x)$ is itself normalized. So

$$\langle E_a \rangle = \int dx \; P(x) \int dv \; \frac{1}{2} m v^2 P(v)$$

$$+ \int dx \; \frac{1}{2} k x^2 P(x) \int dv \; P(v)$$

$$= \int_{-\infty}^{\infty} dv \; \frac{1}{2} m v^2 P(v) + \int_{-\infty}^{\infty} dx \; \frac{1}{2} c x^2 P(x).$$

We recall the trick (3.13–3.14)

$$\int_{-\infty}^{\infty} dy\, y^2 e^{-by^2} = -\frac{d}{db}\int_{-\infty}^{\infty} dy\, e^{-by^2} = \frac{1}{2}\sqrt{\frac{\pi}{b^3}} .$$

So

$$\int_{-\infty}^{\infty} dv\, \frac{1}{2} m v^2 P(v) = \int_{-\infty}^{\infty} dv\, \frac{1}{2} m v^2 \sqrt{\frac{m}{2\pi k T}}\, e^{-\frac{mv^2}{2kT}}$$

$$= \frac{1}{2} m \sqrt{\frac{m}{2\pi k T}} \int_{-\infty}^{\infty} dv\, v^2\, e^{-\frac{m}{2kT} v^2}$$

$$\left(b = \frac{m}{2kT}\right)$$

$$= \frac{1}{2} m \sqrt{\frac{m}{2\pi k T}}\; \frac{1}{2} \sqrt{\pi \left(\frac{2kT}{m}\right)^3}$$

$$= \frac{m}{4} \sqrt{\left(\frac{2kT}{m}\right)^2} = \frac{m}{4}\, \frac{2kT}{m} = \frac{kT}{2} .$$

Similarly,

$$\int_{-\infty}^{\infty} dx\, \frac{1}{2} m x^2 P(x) = \frac{kT}{2} .$$

So $\quad E_a = \frac{1}{2} kT + \frac{1}{2} kT = kT$

as required by the <u>equipartition of energy</u>.