Now $\Delta V = -A$ where $A$ is the area of the piston ($V = AL$). So
\[
\Delta S = \frac{3}{2} \frac{h}{N} \frac{f \delta S}{E} - \frac{N k A \delta S}{AL}.
\]

Now $\frac{E}{N} = \frac{3}{2} k T$, so
\[
\Delta S = \frac{f \delta S}{T} - \frac{N k \delta S}{L} = \frac{\delta S}{T} \left( f - \frac{N k T}{L} \right).
\]

The entropy increases until equilibrium is reached at $L = L_0$ where $\Delta S = 0$
\[
0 = \Delta S = \frac{\delta S}{T} \left( f - \frac{N k T}{L_0} \right).
\]

So $f = \frac{N k T}{L_0}$ and $L_0 = \frac{N k T}{f}$.

Setting $f = pA$ where $p$ is the pressure, we get $pL_0A = pV = N k T$ which is the ideal-gas law.
When a constraint is removed, the number $\Omega$ 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 (gasket spring) can exchange heat with system B, which is a big slab of iron whose temperature $T_B$ remains nearly constant. B is a thermal reservoir.
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

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

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

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

$\Delta V = -A S$, so 

$\Delta S_a = - \frac{NkAS}{AL} = - \frac{NkS}{L}$.  

We must include system B. Now

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

Thus when $S = S_a + S_B$ is maximal

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

$$= -\frac{N k S}{L} - \frac{(-f S)}{T}$$

$$= \frac{S}{T} \left( f - \frac{N k T}{L} \right)$$

which again gives $L_0 = \frac{N k T}{f}$ and

with $f = p A$

$$p V = N k T$$

which is the ideal-gas law. (That was 16c)

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

$$F_a = E_a - T S_a.$$
Here $T$ is the fixed temperature of the thermal reservoir, $F = E - TS$ is the Helmholtz free energy. 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

$$\frac{dF_a}{dL} = \frac{d(E_a - TS_a)}{dL}$$  

$$= -T \frac{dS_a}{dL} = -T \frac{dklnV^N}{dL} = -kNTA \frac{V}{V}$$
So that
\[- \frac{dF_a}{dL} = \frac{kN}{L} = f_a.\]
The force of the rod compressing the
gas is called an entropic force.

The maximum amount of work
system a can do is
\[\int_{L_m}^{L} f_a \, dL = -\int_{L}^{L_m} \frac{dF_a}{dL} \, dL = F(L) - F(L_m).\]

An abstract definition of
pressure \( p \) is
\[p = T \left. \frac{dS}{dV} \right|_E. \tag{6.15}\]

We also have
\[T = \left( \left. \frac{dS}{dE} \right|_V \right)^{-1} = \left( \frac{dS}{dQ} \right)^{-1}. \tag{6.19}'\]
Ideal gas:

\[ S = k \ln E \frac{3N}{2} V \]

\[ \frac{dS}{dV} = \frac{Nk}{V} = \frac{p}{T} \]

So we again get \( pV = NkT \), which is the ideal gas law.

The Gibbs free energy \( G \) is

\[ G = E + pV - TS \tag{6.16} \]

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

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

and the pressure $p$ as

$$p = T \left. \frac{\partial S}{\partial V} \right|_E \tag{6.15}$$

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 $b$.

$$\Delta E_a = -\Delta E_b.$$ 

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

At equilibrium, $0 = \Delta S$

$$0 = \Delta S = \Delta S_a - \frac{\Delta E_a}{T} \quad \text{or} \quad 0 = \Delta \left( -\frac{F_a}{T} \right) = \Delta S_a - \frac{\Delta E_a}{T}.$$ 

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 \( S \) of microstates grow until \( S = S_0 + S_B \) is maximal.

At its maximum,

\[
0 = \Delta S = \Delta S_0 + \Delta S_B.
\]

For small changes of \( E_B \) and \( V_B \)

\[
\frac{1}{T} = \frac{1}{T_B} = \frac{\partial S_B}{\partial E_B} \bigg|_{V_B} \quad \text{and} \quad \frac{p}{T} = \frac{\partial S_B}{\partial V_B} \bigg|_{E}.
\]
So,

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

\[ = \Delta S_a + \frac{1}{T} \Delta E_B + \frac{P}{T} \Delta V_B \]

\[ = \Delta S_a - \frac{\Delta E_a}{T} - \frac{P}{T} \Delta V_a. \]

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

\[ 1 \rightarrow 2 \text{ is isothermal at } T_H, \quad Q_H = T_H \Delta S_{12} \]

\[ 2 \rightarrow 3 \text{ is adiabatic, } T_H \text{ drops to } T_c \]

\[ 3 \rightarrow 4 \text{ is isothermal at } T_c, \quad Q_C = T_c |\Delta S_{34}| \]

\[ 4 \rightarrow 1 \text{ is adiabatic, } T_c \text{ rises to } T_H \]

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 \( T_H = 600^\circ C \approx 900 K \), 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 large system \( B \) is \( S_{2B}(E_B) \). Since \( S_{2B}(E_B) = k \ln S_{B}(E_B) \), it follows that

\[ \ln S_{2B}(E_B) = S_B(E_B)/k \]

or

\[ S_{2B}(E_B) = e^{S_B(E_B)/k}. \]
So the probability of a being in a single microstate of energy $E_A$ and $B$ being in any of the $S_B(E_B)$ microstates of energy $E_B = E - E_A$ is

$$S_B(E_B)/k$$

$$P(E_a) = P_0 S_B(E_B) = P_0 e^{S_B(E - E_A)/k}$$

$$= P_0 e^{S_B(E) - E_A \frac{dS_B(E)}{dE} \frac{dE}{E}}$$

But since

$$\frac{1}{T} = \left. \frac{dS_B}{dE} \right|_0$$

we have

$$S_B(E) = -\frac{E_A}{kT}$$

$$P(E_a) \approx P_0 e^{-\frac{E_A}{kT}}$$

or

$$P(E_a) \approx \text{constant e}$$

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 \( p_1 + p_2 = 1 \). So

\[ \frac{p_1}{p_2} = e^{\Delta E/kT} \]
\[ \Delta E = E_2 - E_1 \]

So
\[ \frac{p_1}{p_2} + 1 = \frac{1}{p_2} = e + 1 \]

and

\[ p_2 = \frac{1}{1 + e} \]
\[ \frac{\Delta E/kT}{1 + e} \]

\[ p_1 = \frac{e^{\Delta E/kT}}{1 + e} = \frac{1}{1 + e} \]
\[ \frac{\Delta E/kT}{1 + e} \]

At high $T$, $p_1 \approx p_2$. But if $E_2 > E_1 + kT$, then $p_2 \approx 0$ and $p_1 \approx 1$. 
Suppose

\[ E_a(x, u) = \frac{1}{2} m u^2 + \frac{1}{2} c x^2. \]

Then

\[ \langle E_a \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_a(x, u) \, P(x, u) \, dx \, du, \]

where

\[ P(x, u) = \frac{N e^{-\frac{E_a(x, u)}{k T}}}{V}, \]

and

\[ N = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{E_a(x, u)}{k T}} \, dx \, du. \]

So

\[ P(x, u) = \left( \sqrt{\frac{m}{2 \pi k T}} e^{-\frac{m u^2}{2 k T}} \right) \left( \sqrt{\frac{c}{2 \pi k T}} e^{-\frac{c x^2}{2 k T}} \right). \]

in which each factor \( P(u) \) & \( P(x) \) is itself normalized. So

\[ \langle E_a \rangle = \int dx \int du \left[ -\frac{1}{2} m u^2 P(u) \right] + \int dx \int du \left[ -\frac{1}{2} c x^2 P(x) \right]. \]
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,

\[
\int_{-\infty}^{\infty} dv \, \frac{1}{2} m v^2 P(v) = \int_{-\infty}^{\infty} dv \, \frac{1}{2} m v^2 \sqrt{\frac{m}{2\pi b T}} e^{-\frac{mv^2}{2bT}}
\]

\[
= \frac{1}{2} m \sqrt{\frac{m}{2\pi bT}} \int_{-\infty}^{\infty} dv \, v^2 e^{-\frac{mv^2}{2bT}}
\]

\[
= \frac{1}{2} m \sqrt{\frac{m}{2\pi bT}} \frac{1}{2} \sqrt{\pi (\frac{2bT}{m})^3}
\]

\[
= \frac{m}{4} \sqrt{(\frac{2bT}{m})^2} = \frac{m}{4} \frac{2bT}{m} = \frac{bT}{2}.
\]

Similarly,

\[
\int_{-\infty}^{\infty} dx \, \frac{1}{2} m x^2 P(x) = \frac{bT}{2}.
\]

So

\[
E_a = \frac{1}{2} kT + \frac{1}{2} kT = kT
\]

as required by the equipartition of energy.