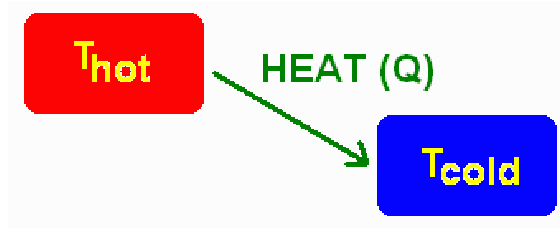
DAY 28

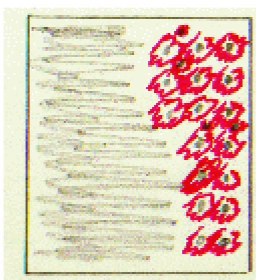
Summary of Primary Topics Covered

The 2nd Law of Thermodynamics

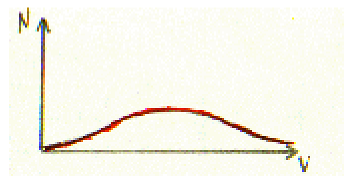


The 2nd Law of Thermodynamics says this – – *Heat energy naturally flows from hotter objects to colder objects.* We know this happens, but why does it have to happen?

Consider a hot object – we'll call it "Object A". In hot objects molecules move rapidly. However, they don't all move rapidly. Some move faster than average; some move slower than average. But because of the shape of the molecular speed distribution, the vast majority of molecules move near the average speed, with relatively few going very fast or very slow.

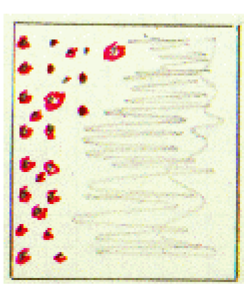


Here the pink indicates violent vibration of molecules in object A, which is hot.

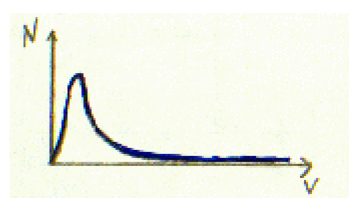


The speed distribution for molecules in object A.

Now think of a cool object that is otherwise identical to A – we'll call this "Object B". In a cool object molecules move slowly. However, they don't all move slowly. Some move slower than average, and a very few move really fast. But because of the shape of the molecular speed distribution, the vast majority of molecules move near the average speed.



Here the pink indicates violent vibration in this solid. Not many are vibrating violently.



The speed distribution for molecules in this cool object.

When the two are put in thermal contact, heat is transferred from one to another via conduction – the direct interaction between molecules.

A  B

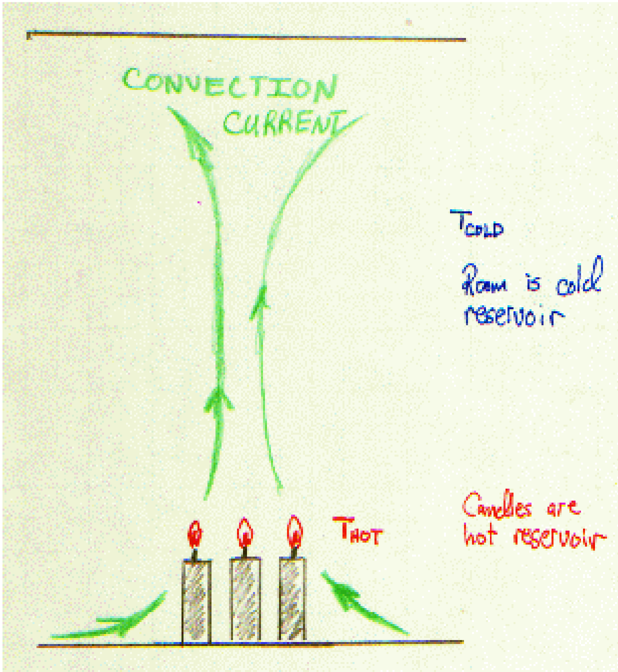
On average, the fast-moving molecules in A are going to transfer some of their energy to the slow-moving molecules in B. The result is that the molecules in B move more violently, and B's temperature increases, and the molecules in A move less violently, and A's temperature decreases. Heat flows from Hot to Cold. This does not mean that occasionally one of B's few fast-movers won't happen to transfer energy to one of A's few slow-movers, but the chances of that happening are very small. In order for heat to flow from Cold to Hot, it would require that all of B's fast-movers just so happened to interact with all of A's slow-movers. The probability of that happening is ridiculously small, given the number of molecules in even as small an object as a grain of sand.

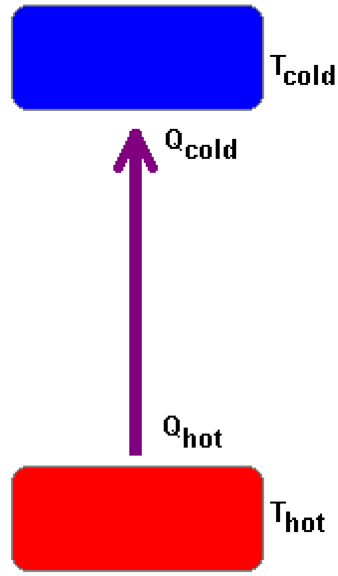
Thus the 2nd Law of Thermodynamics is a law that is based on probabilities and statistics.

Heat Engines

A heat engine is a device that operates in a continuous, cyclic fashion to extract work from the flow of heat from Hot to Cold.

For example, consider candles burning in a cool room. The candles are a thermal reservoir (they can give off heat without cooling down) at high temperature. The room is a thermal reservoir (it can absorb heat from the candles without warming up significantly) at low temperature.

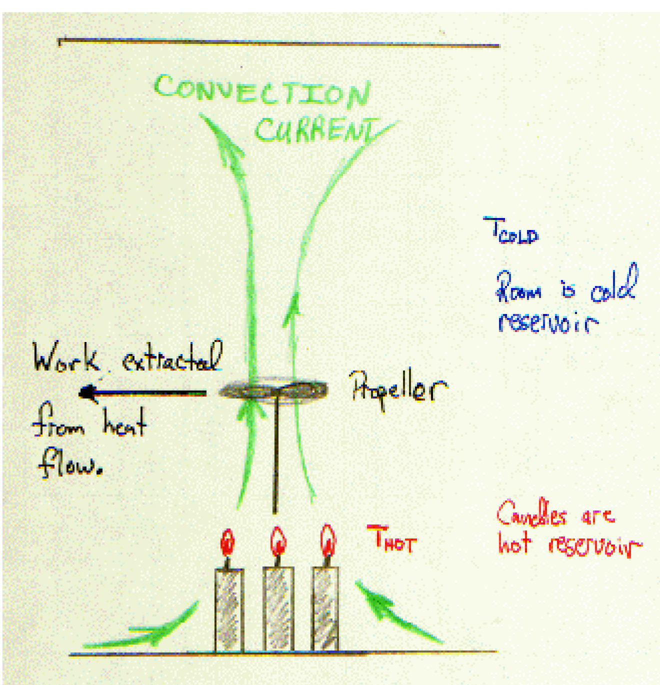


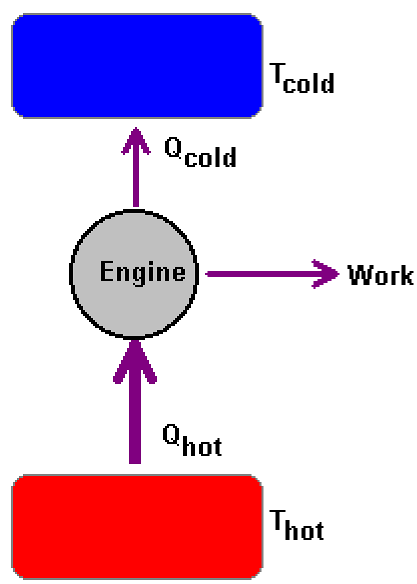


Heat is flowing from Hot to Cold in this system. The heat that leaves the hot candles (Q_{hot}) is equal to the heat that goes into the cold room (Q_{cold}).

$Q_{hot} = Q_{cold}$

Now if we put a turbine (a propeller) in the path of the convection current, we can get work out of the transfer of heat.





This is a heat engine. Now not all the heat energy from the candles goes into the room. Some goes into work, so

$$\mathbf{Q_{hot} = Q_{cold} + Work}$$

Note that there must be a *temperature difference* for the carousel to run. If the whole room is as hot as the candles, the convection won't take place and the engine will not run.

The efficiency of a heat engine is the ratio of work produced to heat from the hot source. It's "what you get" vs. "what you pay for".

$$\mathbf{eff = Work/Q_{hot} = (Q_{hot} - Q_{cold})/Q_{hot} = 1 - Q_{cold}/Q_{hot}}$$

The work produced by an engine depends on the engine's cycle. A heat engine must be able to operate continuously and therefore involves a cyclic process that repeats over and over. In the candle carousel, the cycle is produced by natural convection.

The work produced by an engine depends on the engine's cycle. A heat engine must be able to operate continuously and therefore involves a cyclic process that repeats over and over. In the candle carousel heat engine, the cycle is produced by natural convection. It is fairly complex and tough to analyze mathematically.

However, we can envision an engine with a cycle for which it is easy to calculate work.

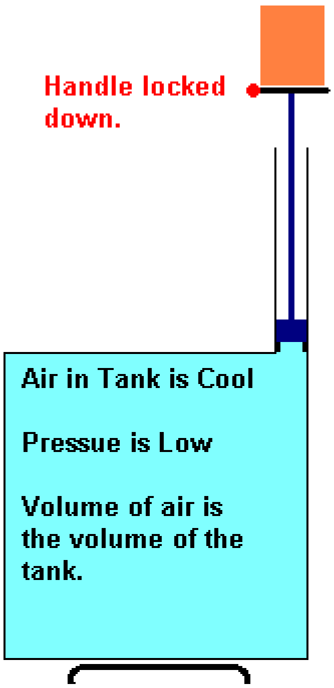
A few terms first:

Isobaric – Constant Pressure
Isochoric or *isovolumetric* – Constant Volume
Isothermal – Constant Temperature
Adiabatic – Negligible heat flow in or out of the system (often because the process occurs too quickly for heat flow to take place, but sometimes because the system is insulated).

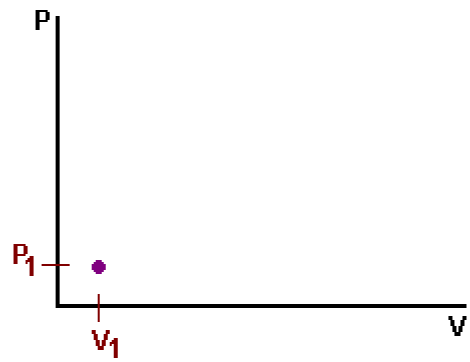
We will use these terms in discussing engine cycles.

Heat Engine Cycles and the P-V Diagram

Imagine an engine that consists of a small bicycle pump attached to a large air tank. A mass sits on the handle of the pump. There is a heater on the tank to help regulate the tank's temperature.



Our cycle begins with the air in the tank at low pressure and temperature.



Initial conditions:

$P = P_1$
$V = V_1$

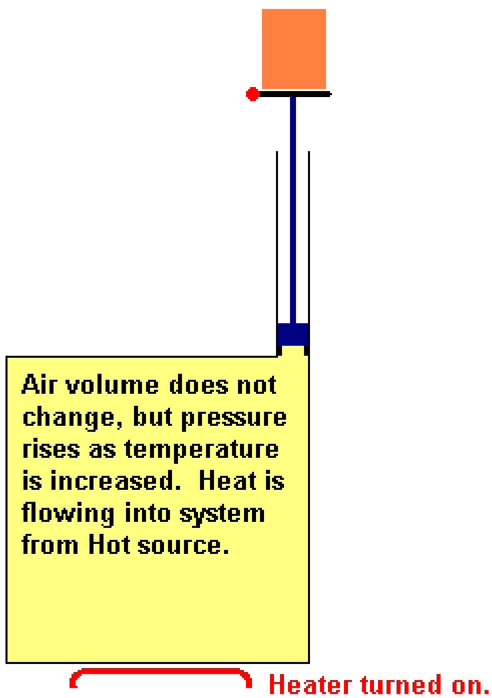
OK, so this doesn't look much like an "engine", especially if "engine" makes you think of something like the picture at right. However, the candle carousel didn't look like an engine, either.

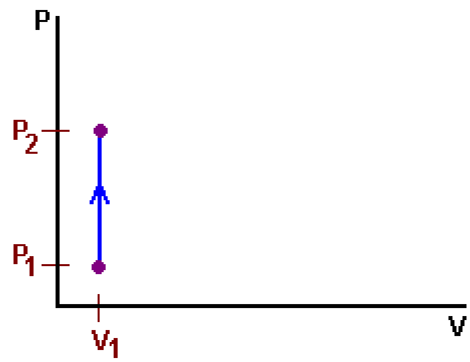
Now we will follow our engine through its cycle.

A really useful engine – and definitely a heat engine.

We begin the cycle by increasing the pressure in the tank. We do this by heating the tank while not allowing the air to expand.

Isochoric pressure increase.





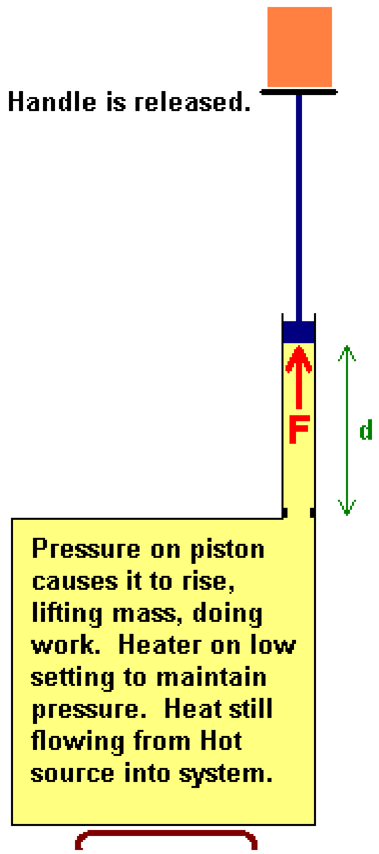
Volume is constant - does not change. Pressure increases.

Conditions at the end of this leg of the cycle:

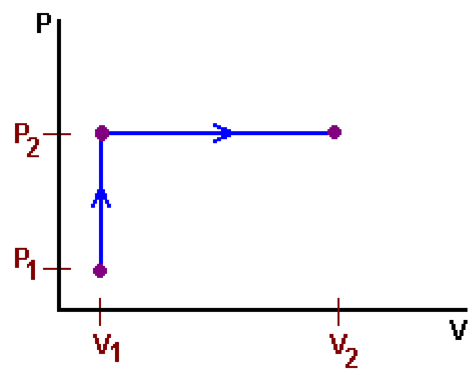
$P = P_2$
$V = V_1$

No work is being done because there is no motion.

The next stage in the cycle will be to release the handle lock and allow the air in the tank to expand while using the heater to heat the air and keep the pressure constant. Expansion under constant pressure is an isobaric expansion…



Isobaric expansion.



Pressure is constant. Volume increases.

Conditions at the end of this leg of the cycle:

$P = P_2$
$V = V_2$

The system is doing work in this leg of the cycle -- the gas expands at constant pressure, lifting the piston:

$$W_{out} = F\ d$$

$$F = P_2\ A$$

$$W_{out} = P_2\ A\ d$$

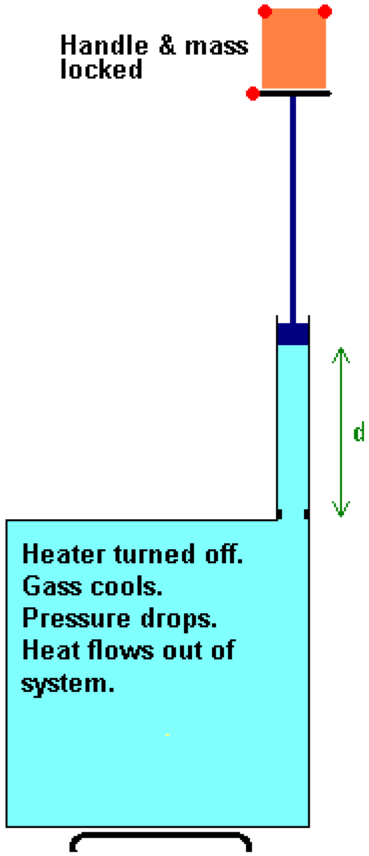
But A d is the volume of the cylinder of the pump. A d is the change in volume of the system.

$$\Delta V = V_2 - V_1 = A\ d$$

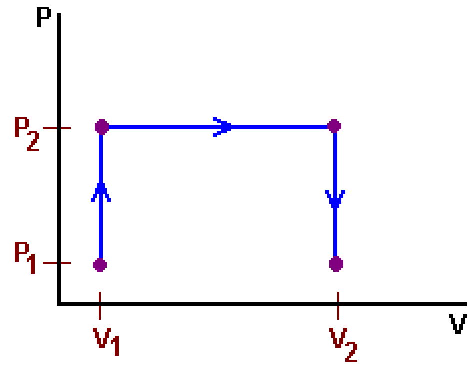
So the work out is

$$W_{out} = P_2\ (V_2 - V_1)$$

Next we will allow the air to cool while holding the volume constant. The pressure will drop, so this is an isochoric pressure decrease…



Isochoric pressure decrease.



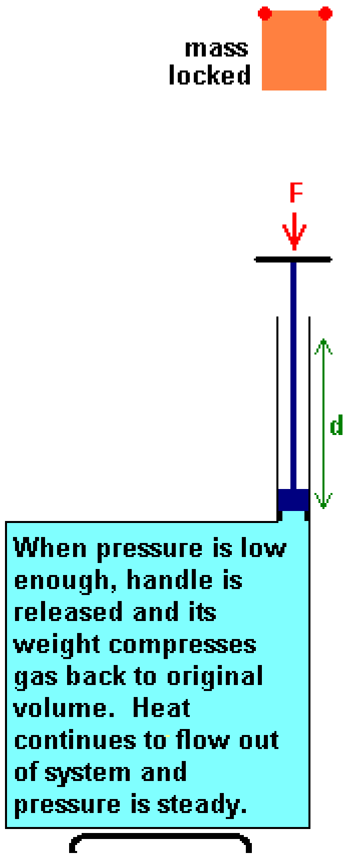
Volume is constant - does not change.
Pressure decreases.

Conditions at the end of this leg of the cycle:

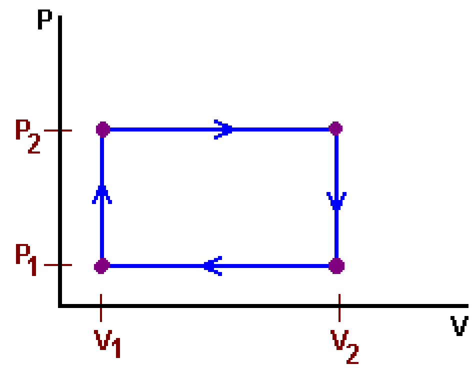
$P = P_1$
$V = V_2$

No work is being done because there is no motion.

The next stage in the cycle will be to again release the handle lock. We will allow the air in the tank to cool and contract back to its original volume under the weight of the handle. This keeps the pressure constant. This is an isobaric compression…



Isobaric compression.



Work is not being put out by the system – the gas is being compressed so work is going in to the system:

$$W_{in} = F\ d$$

$$F = P_1\ A$$

$$W_{in} = P_1\ A\ d$$

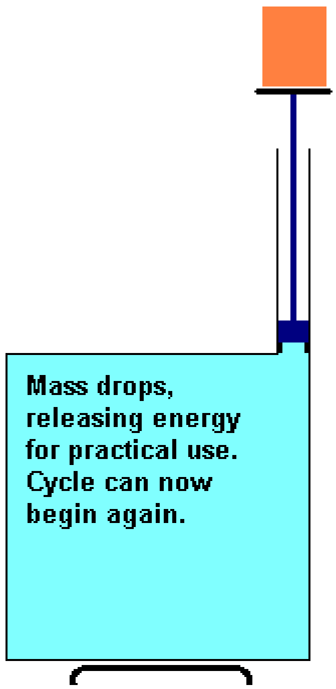
But A d is the volume of the cylinder of the pump. A d is the change in volume of the system.

$$\Delta V = V_2 - V_1 = A\ d$$

So the work in is

$$W_{in} = P_1\ (V_2 - V_1)$$

At this point we can release the mass and let it fall. This gets us back to our starting point …



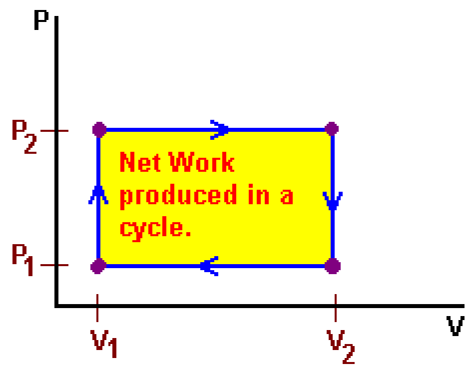
The total work produced in one cycle of this engine is

$$W_{cycle} = W_{out} - W_{in}$$

$$= W_{out} = P_2 \ (V_2 - V_1) - P_1 \ (V_2 - V_1)$$

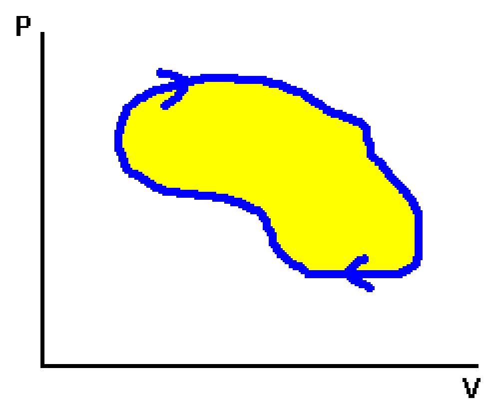
$$= (P_2 - P_1)(V_2 - V_1)$$

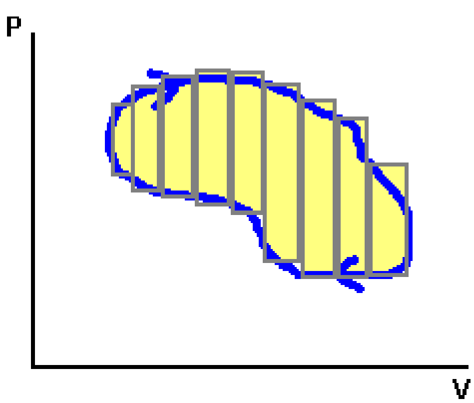
This is the same as the area enclosed by the rectangle traced out on the P-V diagram.



This is a general result – *the work done by a heat engine over one cycle is the area enclosed by that cycle's curve as plotted on a P-V diagram*.

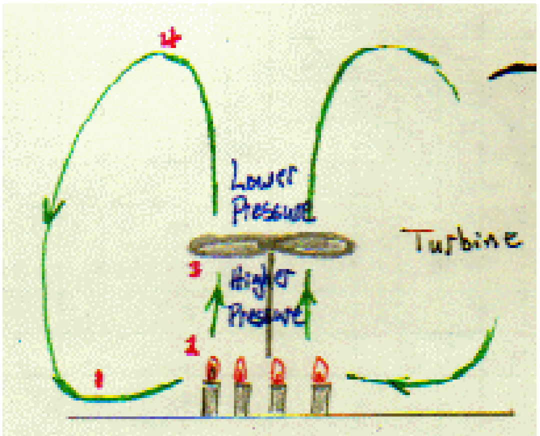
This is a general result because any cycle, even something like the weird-looking cycle at right, can be approximated by a series of rectangles.

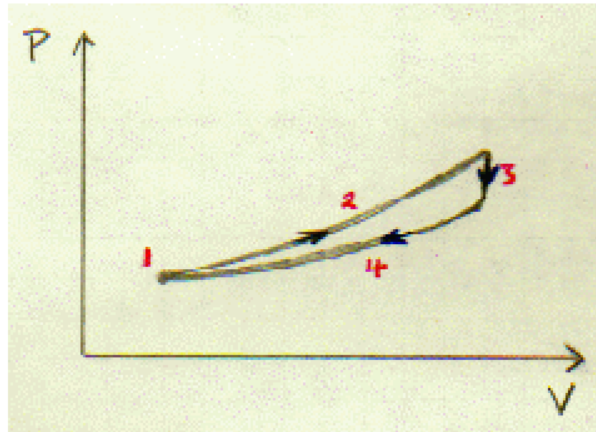




In calculus, in the limit where these rectangles are infinitesimally small, the approximation becomes exact, and the work is found by "integrating" to find the area enclosed by the cycle on the P-V diagram.

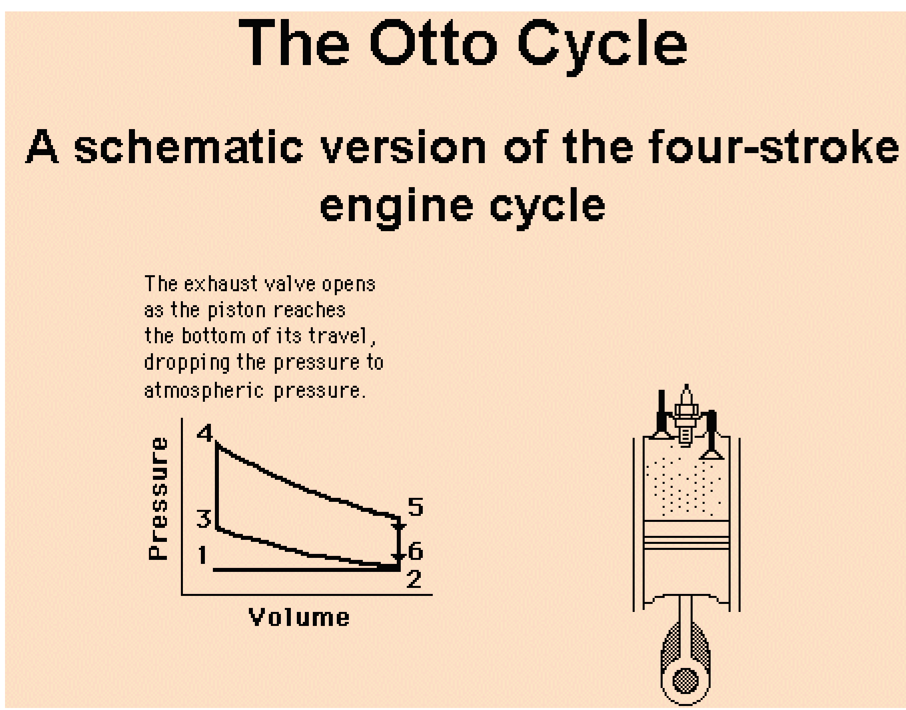
Different types of engines use different cycles. In class we demonstrated a candle carousel. The cycle of our candle carousel (which is a sort of turbine) looks something like this:





A convection current drives the candle carousel engine. Cool air under low pressure (1) is drawn to the flames, where it is heated and expands (2). The air then rises against the underside of the turbine. The air above the turbine is at slightly lower pressure, and the pressure difference causes air to pass through the turbine and spin the turbine. When the air passes through the turbine its pressure drops slightly (3). The air then cools and contracts (4) and the cycle starts again.

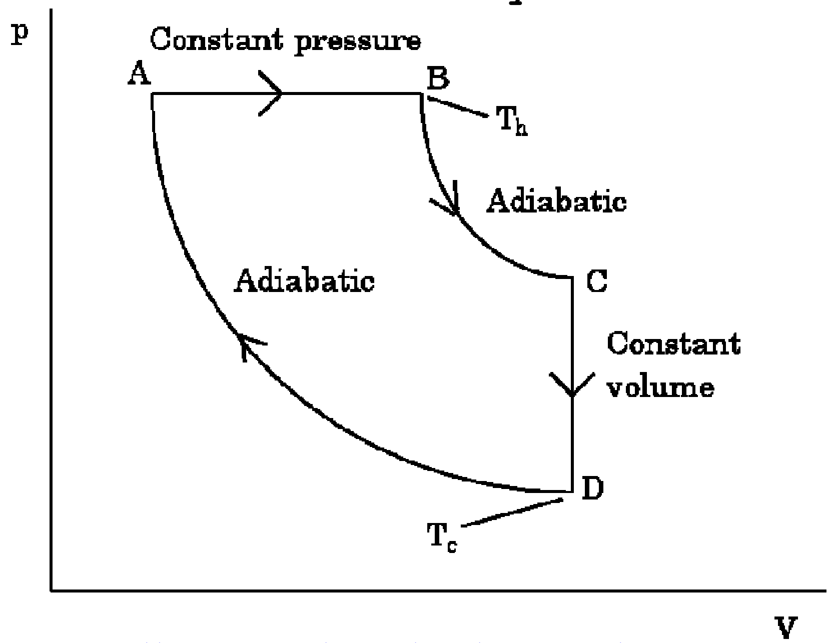
A "four-stroke" gasoline engine (the kind that powers our cars), operates on the *Otto Cycle*.



http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/otto.html#c5

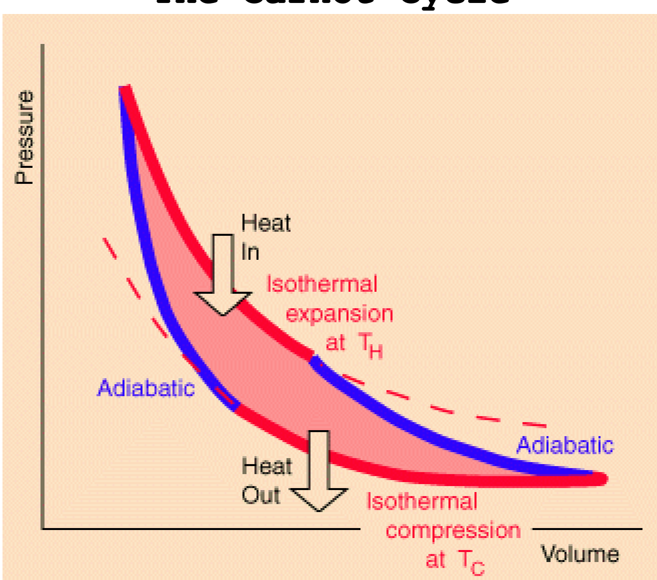
A Diesel engine (the kind that powers railroad locomotives and big trucks), operates on the *Diesel Cycle*.

The Diesel Cycle



http://he.daveb.net/phys47/html/latex2html/node95.html

The Carnot Cycle



http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/carnot.html#c1

The most efficient cycle possible is known as the *Carnot Cycle*. It can be proven that no engine can be more efficient than a Carnot engine (that proof is beyond the scope of our course – even the calculus version).

Carnot engines are not practical to build, so we use things like 4-stroke and Diesel engines instead. However, the efficiency of a Carnot engine marks an upper limit for the efficiency of any engine.

We can get a "seat of the pants" feel for Carnot efficiency by remembering that

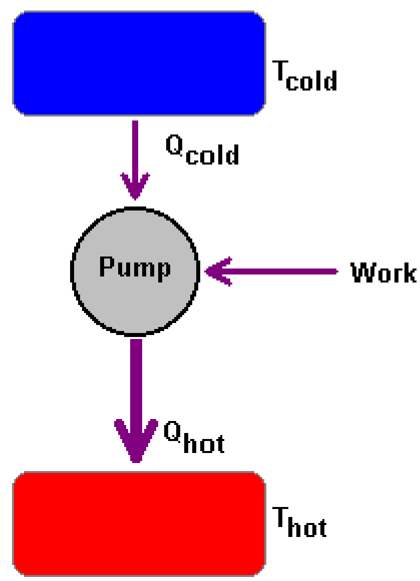
$$\text{eff} = 1 - Q_{cold}/Q_{hot}$$

and thinking of the candle carousel. If the room was colder then the convection currents would be stronger so long as the candle temperature was the same. This is because buoyant effects would be greater. A cooler room would mean more efficient operation. Likewise, hotter candles would have the same effect. Knowing that temperature affects efficiency, and knowing the efficiency formula, perhaps we can see how the efficiency of a Carnot engine operating off a high-temperature reservoir with temperature T_{hot} and exhausting heat into a low-temperature reservoir with temperature T_{cold} would be

$$\mathbf{eff_{Carnot} = 1 - T_{cold}/T_{hot}}$$

(Here the temperatures are in absolute units.) That's not a real derivation, but it will have to do.

Heat Pumps and the Many Forms of the 2nd Law of Thermodynamics

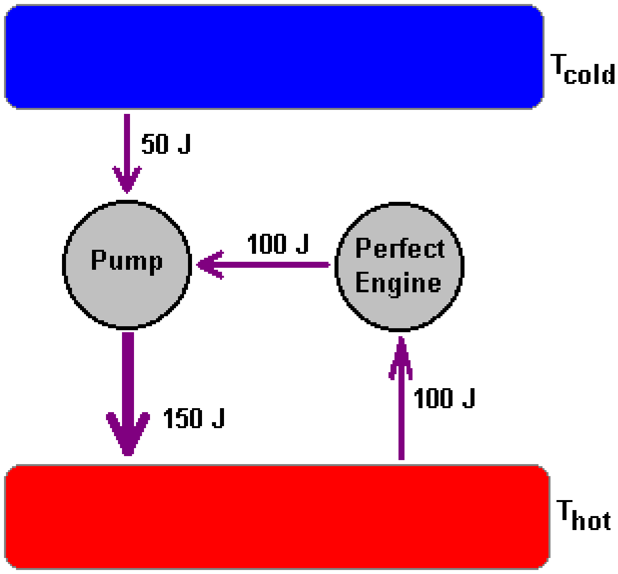


A heat pump (also known as a refrigerator or air conditioner) is a device that operates in a continuous, cyclic fashion and uses work to get heat to flow from Cold to Hot. Note that a heat pump is essentially a heat engine in reverse (the engine is a device that operates in a continuous, cyclic fashion to extract work from the flow of heat from Hot to Cold).

There can be no such thing as a perfect heat pump – one that would cool your home with no work (in other words, A/C with no electric bill). That's because a perfect heat pump would mean the free flow of heat from Cold to Hot, and the 2nd Law of Thermodynamics says that does not happen.

So, the 2nd Law of Thermodynamics says this – *A Perfect Heat Pump is not possible.*

But this statement implies that a perfect, 100% efficient engine is not possible. Why does it imply that? Suppose you had a perfect engine – one that could take 100 J of heat from a hot source and turn it into 100 J of work. Then you fed that 100 J of work into a regular heat pump, which used that 100 J to pull 50 J of work out of a cold source and exhausted 150 J of heat back into your hot source:



The bottom line is that you moved that 50J of heat out of the cold place for no net work – essentially a spontaneous flow of heat from cold to hot, in violation of the 2nd Law of Thermodynamics. That can't happen, so a perfect engine is not possible.

So, the 2nd Law of Thermodynamics says this – *A Perfect (100% efficient) Heat Engine is not possible.*

This also rules out the possibility of having a temperature of absolute zero. That's because

$eff_{Carnot} = 1 - T_{cold}/T_{hot}$

and if $T_{cold} = 0$ you'd have $eff_{Carnot} = 100\%$. That would be a perfect engine, and we just saw that perfect engines are not possible.

So, the 2nd Law of Thermodynamics says this – *Absolute zero (T = 0 Kelvin or T = 0 Rankin) cannot be reached.*

Scientists have achieved temperatures of less that a hundredth of a Kelvin in the laboratory, but they have never achieved absolute zero.

The Arrow of Time

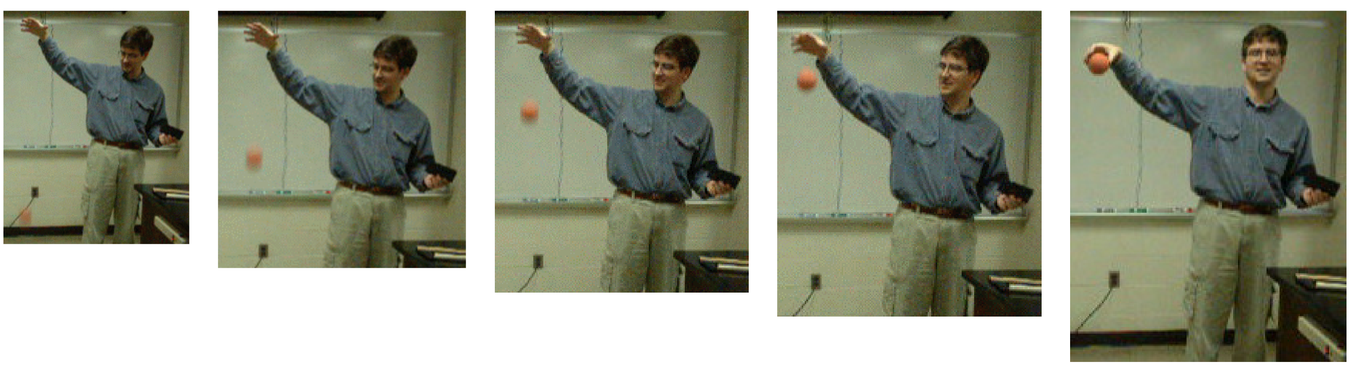
Finally, the nature of the 2nd Law defines the flow of time. The movement of heat from Hot to Cold is a movement from a state of relative order (hot object with fast moving molecules and more energy on one side, cold object with slow molecules and less energy on the other) to a state of relative disorder (everything uniform and intermixed).

Disorder is measured by a quantity known as *entropy* – more disorder means greater entropy, and the movement of heat from hot to cold results in an increase in entropy.

So, the 2nd Law of Thermodynamics says this – *The entropy of the universe naturally increases – nature tends toward disorder.*

This actually extends beyond the flow of heat. A deck of cards, when purchased, is ordered (A 2 3 … of Spades; A 2 3 … of Hearts; A 2 3 … of clubs; A 2 3 … of diamonds). A couple of shuffles results in disorder. A couple of more shuffles will not re-order the deck! That is because the rules of probability govern card shuffling just like they govern heat flow. An ordered deck is much less probable than a disordered deck just like the flow of heat from Cold to Hot is much less probable than the flow of heat from Hot to Cold. Likewise, a couple of little kids turned loose in a room of neatly shelved toys will result in complete disorder in a 15 minutes. Waiting another 15 minutes will not result in the room straightening itself up. It is possible to cause entropy to decrease in a localized area (you can clean up the room), but only at an expense of energy that causes an overall increase in entropy for the universe as a whole.

This tendency toward disorder, which occurs nearly any time other forms of energy are converted to heat, indicates the flow of time. Processes which do not involve dissipating energy into heat or creating disorder appear *reversible* in time. For example, is the sequences of images below of a professor catching an upward-moving ball?



Or is it a sequence of images of a professor dropping the ball, arranged in time-reverse order? The fact is, it could be either. The flow of time is not definite in this case. However, there's no doubt that the next sequence of frames is in time-reverse order.

Why? Because we see disorder move into order. We see an airbag retract into the steering wheel. We see the 2^{nd} Law of Thermodynamics being violated.

And so we end the class, having seen just what defines the flow of time!

Example Problem #1:

A heat engine whose efficiency is 40% produces a 1 Hp output. Calculate the heat used by the engine in 1 minute.

1 Hp = 746 Watts or 746 J/s
So in one minute (60 seconds) the engine produces
W = 746 J/s (60 s) = 44,760 J of work.

$Eff = Work/Q_{hot} = 40\% = .40$
$(44{,}760\ J)/Q_{hot} = .40$

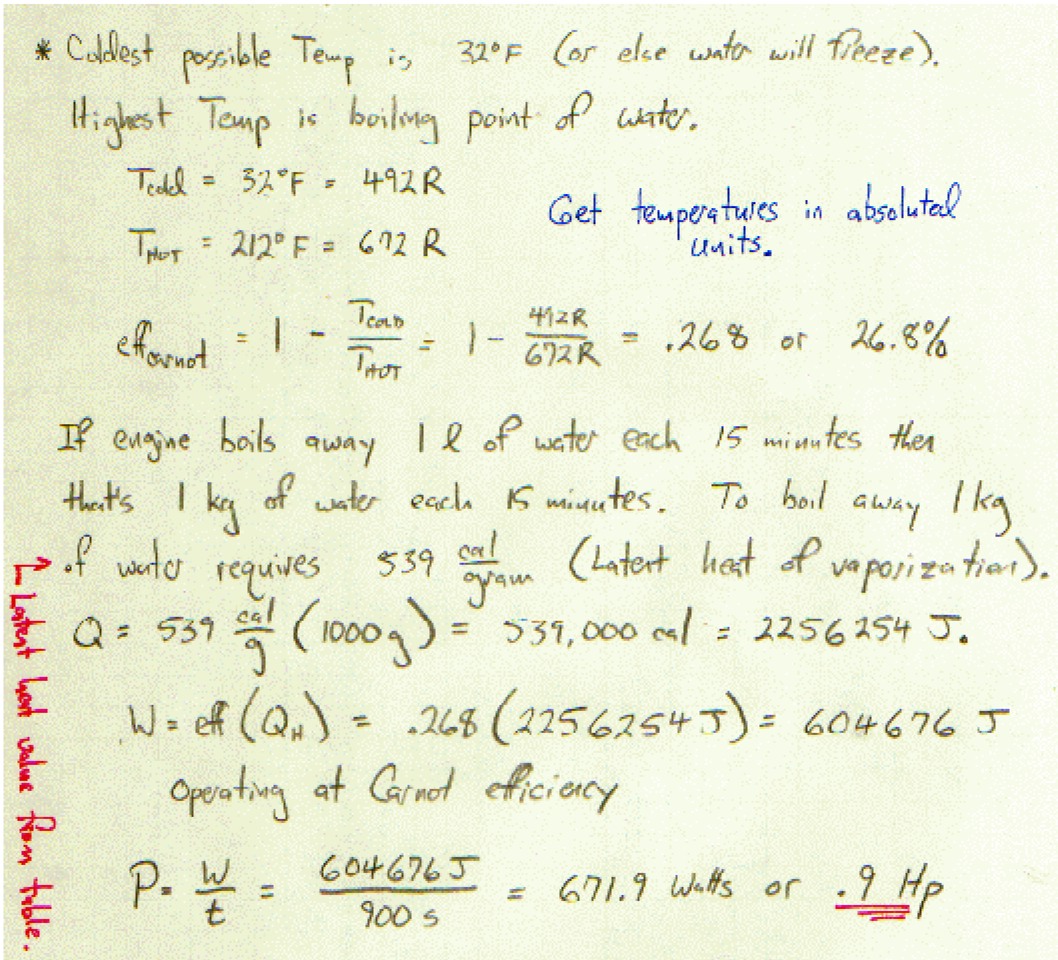
$(44{,}760\ J)/.40 = Q_{hot}$

$111{,}900\ J = Q_{hot}$

The engine uses 111.9 kJ of heat in one minute.

Example Problem #2:

Estimate the maximum possible efficiency of a steam engine. If a steam engine with maximum efficiency boils away water at a rate of 1 liter every 15 minutes, what is its power output?



* Coldest possible Temp is 32°F (or else water will freeze).
Highest Temp is boiling point of water.

T_{cold} = 32°F = 492R
T_{HOT} = 212°F = 672 R

Get temperatures in absolute units.

$eff_{carnot} = 1 - \frac{T_{COLD}}{T_{HOT}} = 1 - \frac{492R}{672R} = .268$ or 26.8%

If engine boils away 1 ℓ of water each 15 minutes then that's 1 kg of water each 15 minutes. To boil away 1 kg of water requires 539 $\frac{cal}{gram}$ (Latent heat of vaporization).

← Latent heat value from table.

$Q = 539 \frac{cal}{g}(1000g) = 539{,}000$ cal = 2256254 J.

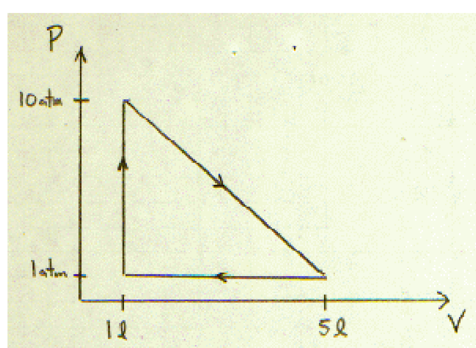
$W = eff(Q_H) = .268(2256254 J) = 604676$ J

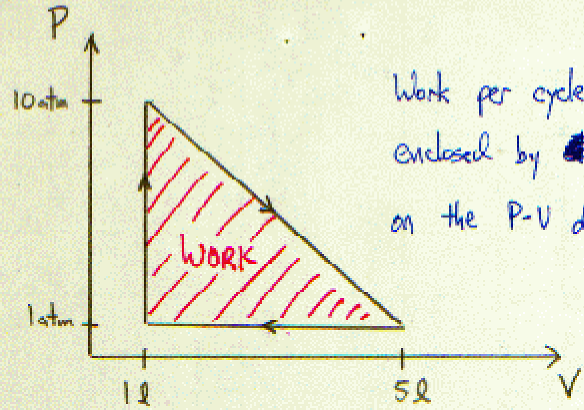
Operating at Carnot efficiency

$P = \frac{W}{t} = \frac{604676 J}{900 s} = 671.9$ Watts or .9 Hp

Example Problem #3:

What is the work done by an engine that operates on the cycle shown at right?





Work per cycle is area enclosed by cycle on the P-V diagram.

This is a triangle with base of 4ℓ and height of 9 atm.

$A = \frac{1}{2}bh = \frac{1}{2}(4\ell)(9\text{ atm}) = \text{Work}$

$\text{Work} = 18\ \ell\cdot\text{atm}$

$= 18\ \ell\cdot\text{atm}\left(\frac{1\ \text{m}^3}{1000\ \ell}\right)\left(\frac{1.01\times10^5\ \frac{\text{N}}{\text{m}^2}}{1\ \text{atm}}\right)$

$= 1818\ \text{N}\cdot\text{m}$

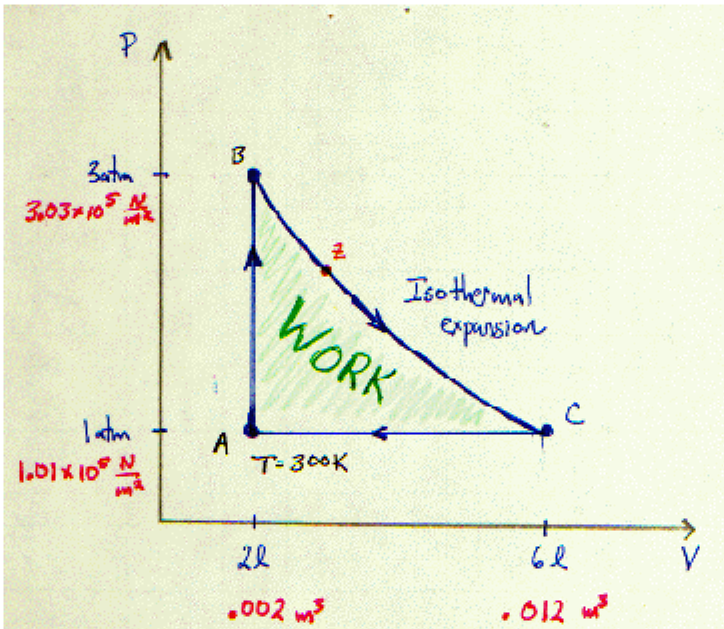
$= 1818\ \text{J}$

PHY 231 ONLY

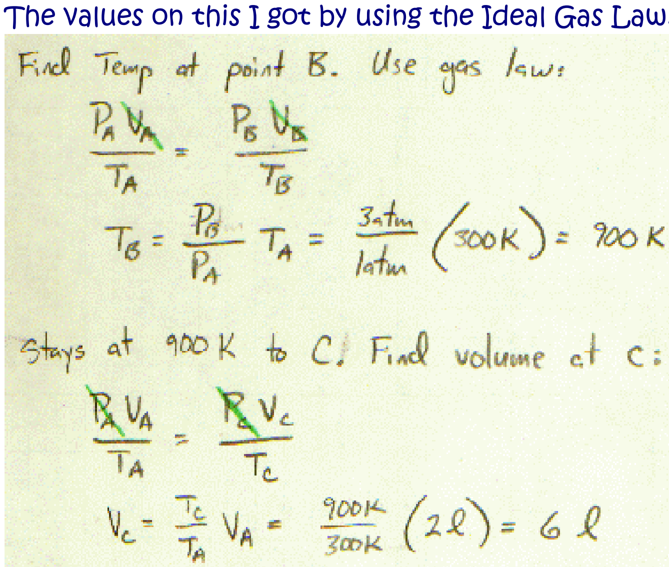
Example Problem #4:

A gas occupies 2 liters at atmospheric pressure and 300 K. It is heated isochorically until it reaches 3 atm pressure. Then it expands isothermally until its pressure drops back to 1 atm. Finally, it is compressed isobarically to its original state. Find the work done by this cycle.

First I create the P-V diagram at below:



The values on this I got by using the Ideal Gas Law. Here are my calculations:



Find Temp at point B. Use gas laws:

$$\frac{P_A V_A}{T_A} = \frac{P_B V_B}{T_B}$$

$$T_B = \frac{P_B}{P_A} T_A = \frac{3atm}{1atm}(300K) = 900K$$

Stays at 900 K to C. Find volume at C:

$$\frac{P_A V_A}{T_A} = \frac{P_C V_C}{T_C}$$

$$V_C = \frac{T_C}{T_A} V_A = \frac{900K}{300K}(2\ell) = 6\ \ell$$

Now I find work done by finding area enclosed by the cycle on the P-V diagram:

Finding area under the isotherm curve require integrating:
Need equation for P as function of V:

At some point Z:

$$\frac{P_B V_B}{T_B} = \frac{P_Z V_Z}{T_Z} \qquad T_Z = T_B \text{ because it's an isotherm.}$$

$$(3\,atm)(2\,\ell) = P_Z V_Z$$

$$P_Z = \frac{6\,\ell\,atm}{V_Z}$$

There's my equation – now integrate to find area.

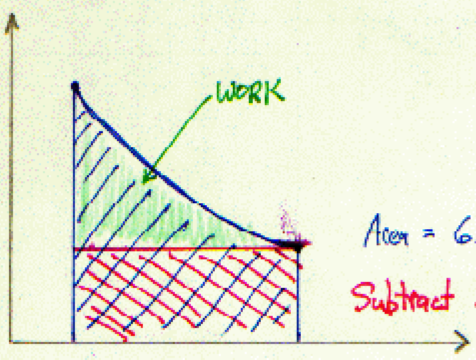
$$Area = \int_A^C P_Z\,dV = 6\,\ell\,atm \int_{2\ell}^{6\ell} \frac{1}{V_Z}\,dV$$

$$= 6\,\ell\,atm\,\ln V_Z \Big|_{2\ell}^{6\ell}$$

$$= 6\,\ell\,atm\,(\ln 6\ell - \ln 2\ell)$$

$$Area = 6\,\ell\,atm\,\ln\left(\frac{6\,\ell}{2\,\ell}\right) = 6.592\,\ell\,atm$$

But the area under the isotherm curve is not the area enclosed. I have to do a little subtraction to get the area enclosed, which is the work done:



Area = 6.592 ℓ atm

Subtract off this area = 4 ℓ atm

WORK = 2.592 ℓ atm

$$2.592\,\ell\,atm \left(\frac{1\,m^3}{1000\,\ell}\right)\left(\frac{1.01\times10^5\,N/m^2}{1\,atm}\right) = 262\,J$$

So the work done in one cycle is 262 J.

Example Problem #5:

Suppose an airtight room that measures 3 m high by 5 m wide by 12 m long has a glass wall down the center. One half of the room is filled with air at atmospheric pressure at a temperature of 20°C. In the other half of the room is a vacuum. When the glass is broken, the air will expand to fill the room. The expansion happens rapidly, so little heat can flow in or out. This is an example of the 2nd Law of Thermodynamics in action – an ordered system (room half full of air, half empty of air) rapidly tends toward a more disordered system (air molecules scattered throughout the room).

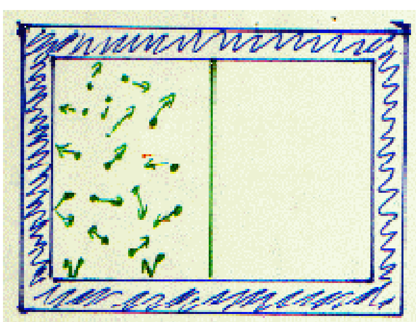
A) Is this process an isothermal, isochoric, isobaric, or adiabatic process?

B) What is the probability that the 2nd Law of Thermodynamics will be violated and that the air in the room will spontaneously re-order itself into the state it was in before the glass was broken?

Part (A) is easy. Since negligible heat flows in or out of the room during the expansion, this is an <u>adiabatic</u> process.

Part (B) is tougher. Air molecules move randomly. So once the glass is broken, any one air molecule has a 50% (that is a probability of Pr = ½) chance of being found in the half of the room that was originally a vacuum, and a 50% (Pr = ½) chance of being found in the half of the room that originally contained the air.

Let's say that before the class was broken the air molecules were on the left side of the room:



Now I'll figure some probability stuff:

Probability of 1 molecule being in left-hand side of room is $\frac{1}{2}$

$$P_1 = \frac{1}{2} = \left(\frac{1}{2}\right)^1$$

Probability of two molecules both being in left-hand side of room is $\frac{1}{2} \times \frac{1}{2}$

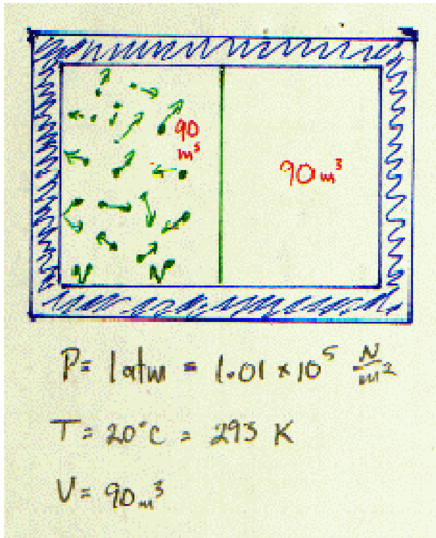
$$P_2 = \frac{1}{4} = \left(\frac{1}{2}\right)^2$$

Probability of N molecules being in left-hand side of room is

$$P_N = \left(\frac{1}{2}\right)^N$$

So, to find Pr_N I need to find N, the number of molecules in the room. I can do this using the Ideal Gas Law and the temperature and volume of the room.

Room Volume = 3 m × 5 m × 12 m = 180 m^3



Using Ideal Gas Law:

$$PV = NkT$$

$$N = \frac{PV}{kT}$$

$$N = \frac{\left(1.01\times10^{5}\,\frac{N}{m^2}\right)\left(90\ m^3\right)}{\left(1.38\times10^{-23}\,\frac{J}{K}\right)\left(293\ K\right)}$$

$$= \frac{9.09\times10^{6}\ Nm}{4.04\times10^{-21}\ J}$$

$$N = 2.25\times10^{27}\ \text{molecules}$$

Now I have my N value so

So for this room, the probability that the air in the room will spontaneously return to its previous, ordered state is

$$Pr = \frac{1}{2^{2.25 \times 10^{27}}}$$

So the chances that the air in the room will spontaneously return to the left half of the room, to the state it was in before the glass was broken is 1 in

$$2^{2.25 \times 10^{27}} = \left(2^{2.25}\right)^{10^{27}} = 4.75^{10^{27}} = 5{,}854{,}361^{27}$$

The chances are 1 in $(5{,}850{,}000)^{27}$

(i.e. it isn't going to happen)

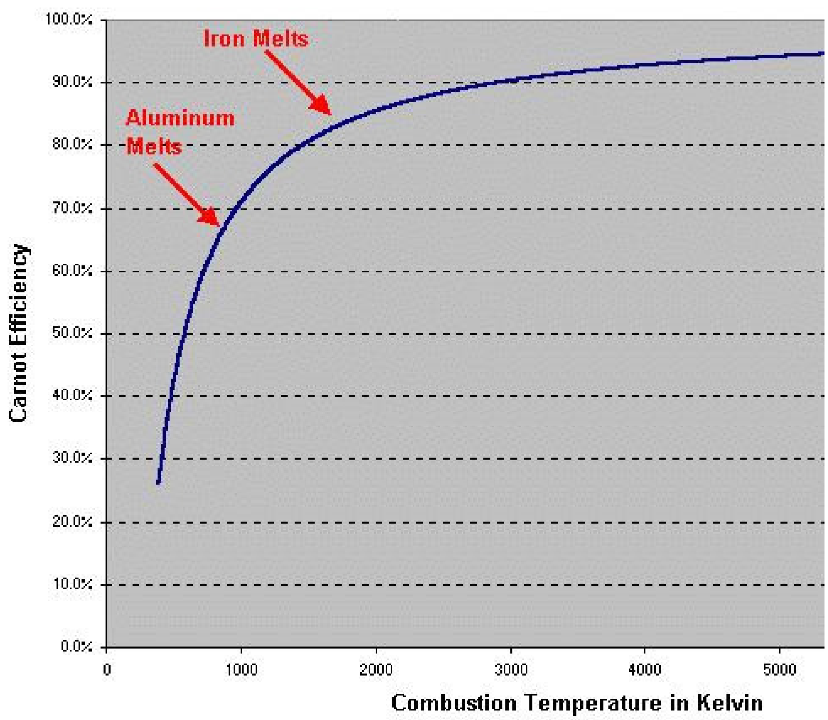
By comparison, a one in a billion chance means the chances are 1 in $(5{,}850{,}000)^{1.33}$. A 1 in a trillion chance means the chances are 1 in $(5{,}850{,}000)^{1.78}$. This <u>really</u> isn't going to happen!!!

Example Problem #6:

Heat engines designed to run cars and planes must exhaust heat into the atmosphere (temperature of about 65°F). The temperature at which they burn their fuel determines their maximum efficiency. Make a plot of Carnot Efficiency vs. combustion temperature for an atmosphere temperature of 65°F. Look up the melting points of various metals that might be used in engines. An engine cannot melt, so mark on your plot where these melting points are. Why do you suppose talk of building high-efficiency engines often involves using ceramic components? Discuss this and your plot.

The atmosphere is our cold temperature source, so T_{cold} = 65°F = 525 R = 292 K

So I need to plot $eff_{Carnot} = 1 - (292/T_{Hot})$



I've added points for the melting temperatures of aluminum and iron, which I found in the table of latent heats. Of course a metal can't really be near its melting point in an engine, and real engines don't reach their Carnot efficiencies. However, I can see two things here. One is that higher temperatures yield higher efficiencies. Ceramics can withstand high temperatures so that's probably why they are being looked at in high-efficiency engines. The other is that eventually further increases in temperature don't gain you that much in efficiency. Once you pass the 70% efficiency mark you really have to run the temperature up to get much higher efficiency out of the engine.