

## Some useful ideas from thermodynamics.

GFD-1 emphasizes the physical dynamics of density-stratified fluids on the rotating Earth, and is basic to the understanding of atmospheric and oceanic circulation, waves and instabilities. Energy is *supplied* to the system principally by solar radiation, but also by a weak geothermal heating and by tidal forcing. Thermodynamics thus plays a central role, across the whole range of length scale of these circulations. Mechanical energy is *dissipated* (converted to heat, usually) by very small-scale velocity gradients, which we saw in Fall Q. labs, where the kinetic energy in a stirred bathtub disappeared after a few tens of seconds (after about 1 rotation of the most energetic, large eddies). This was vastly faster dissipation than the time (days to weeks) for simple viscous diffusion to destroy the large eddies directly.

*Some basic thermodynamics: what is temperature?* The 1<sup>st</sup> law of thermodynamics is the key energy equation for thermal energy. We want to discuss what we mean by the temperature, T. Too often, textbooks introduce temperature without defining it. This is likely because the science of thermodynamics was developed before atoms and molecules were identified. The equation of state,

$$p = \rho RT$$

where p is pressure (Newton m<sup>-2</sup>),  $\rho$  is density (kg m<sup>-3</sup>) and T is temperature (in Kelvin degrees written K (not °K), K = °C + 273.15). R is the gas constant, discussed below.

The equation of state can be derived from classic kinetic-molecular theory by equating the *momentum flux* carried by the molecules to the pressure. One way to do this is for molecules bouncing elastically off a plane boundary, equating the change in their momentum to the (time-integrated) normal force they exert on the boundary. An equivalent way, avoiding questions of the elastic reflection of the molecules, is to find the flux of momentum past a fixed control plane in the midst of the fluid, say at position x=0, without any rigid boundary. As with any substance, the flux of something is the density of the substance (amount per m<sup>3</sup>) times the velocity normal to the control plane. If x-component of velocity is  $u_1$ , the density of x-momentum is  $\rho u_1$  and the flux of x-momentum in the x-direction (per m<sup>2</sup> of the surface) is

$$\rho u_1^2 \quad (\text{kg m}^{-1}/\text{sec}^2).$$

Molecules are whizzing in both directions, the ones with positive  $u_1$  carry their momentum to the right and the ones with negative  $u_1$  carry negative momentum to the left; both contribute to an increase in x-momentum to the right of x = 0 and an increase in negative x-momentum to the left. Equilibrium can be established by putting the gas in a box with reflecting walls.

We call this momentum flux per unit area the pressure, p (newton m<sup>-2</sup>  $\equiv$  kg m<sup>-1</sup> sec<sup>-2</sup>....just use F = MA to check units), a momentum flux per unit area across the plane x=0. It is also the force per unit area exerted normal to a *solid* boundary (one which does not heat or cool the gas, but merely reflects molecules). But, somewhat mysteriously, momentum flux is also equal to twice the kinetic energy density contributed by the x-velocity,  $KE_1 = \frac{1}{2}\rho u_1^2$ . This is related to the situation in Bernoulli's equation, which is derived as an integral of the momentum equation along a streamline, but becomes an energy equation.

We are almost there. First notice that molecules have velocity in all 3 directions, so the total kinetic energy density (per unit volume) is  $KE = 3KE_1$  and thus

$$p = 2 KE_1 = 2/3 KE \quad (\text{Joules m}^{-3} = \text{kg m}^{-1} \text{ sec}^{-2}).$$

Now *define* the temperature as a constant times the kinetic energy per kg. of gas,  $KE/\rho$  (Joules  $kg^{-1}$ ) :

$$T = \frac{2}{3} \frac{KE}{\rho R} \Rightarrow p = \rho R T \quad (8)$$

Thus *temperature is defined as*  $(2/3R)$  times the molecular kinetic energy per kg of gas,  $KE/\rho$ . Since  $R$  varies for different species of gas, we show below that *temperature  $T$  is also a constant times the kinetic energy of a single gas molecule.*

The value of  $R$  depends on the gas in question but relates simply to a universal constant

$$R^* = 8314.36 \text{ (J kmole}^{-1} \text{ K}^{-1} \text{)},$$

through

$$R = R^*/m_a$$

where  $m_a$  is the mass in grams of one mole of gas (that's  $6.02 \times 10^{23}$  molecules, Avogadro's number) while  $m$  is the mass of single molecule. For air, dominantly nitrogen (78% by mass) and oxygen (21%),  $m_a$  averages to  $28.97 \text{ (g mole}^{-1} \text{)}$  and so  $R = 8314.36/28.97 = 287.04 \text{ (J. kg}^{-1} \text{ K}^{-1} \text{)}$  (Gill, p.40). Recall that one mole of gas would occupy 22.4 liters of volume at standard temperature and pressure ( $0^\circ \text{C}$ , 1 atmosphere pressure).

The temperature, therefore, is proportional to the mean kinetic energy per kg of gas: thermal energy is microscopic, molecular, mechanical KE. This gives us an immediate way of knowing how fast these molecules travel. Inverting the result above, the root-mean-square speed (averaging indicated by brackets  $\langle \rangle$ ) is

$$\langle |u|^2 \rangle^{1/2} = (3RT)^{1/2} \quad (\text{or, } = (3R^*T/m_a)^{1/2}). \quad (*)$$

which for air at room temperature ( $T = 300\text{K}$ ) is a speed of  $508 \text{ m sec}^{-1}$ . This is particularly interesting, because it is barely faster than the speed of sound in air ( $347 \text{ m sec}^{-1}$  at  $300\text{K}$ ). Anyway it's a view of the molecular world obtained by rather simple arguments and measurement of pressure and air density alone.

*Different species of air have different molecular speeds.* While this molecular speed is an often cited result of classical ideal gas theory, it ignores the differences among the various molecular species making up the gas. In a gas like air made of several molecular species, an additional result of statistical mechanics is that the frequent elastic collisions of molecules with one another cause the kinetic energy per molecule to be the same for each species....equipartition of energy. This means that the lighter molecules are moving faster; in some cases much faster: from eqn. (\*) the ratio of mean speeds varies as  $(\text{ratio of masses})^{-1/2}$ ; think of billiard balls colliding with bowling balls. Thus the mean speed of helium atoms, with atomic mass  $4 \text{ g mole}^{-1}$  in the atmosphere, at room temperature, is about  $1370 \text{ m sec}^{-1}$ . In fact some light molecules in the atmosphere escape the Earth's gravity field. These are not the 'average' molecules, but the fastest ones at the tail of the Gaussian distribution of molecular velocity, exceeding  $10 \text{ km sec}^{-1}$ . Hydrogen and helium tend to escape, whereas on Jupiter's atmosphere, with its stronger gravity field, these species are abundant. Very high in the atmosphere (above about  $200 \text{ km}$ ) the composition of air becomes dominated by light molecules or atoms.

Most texts on the subject write this result in terms of Boltzmann's constant,  $k_B = 1.38 \times 10^{-23} \text{ (Joules per molecule per degree K)}$ , whereupon the kinetic energy of a single molecule (in a simple gas with just one species) is

$$KE_{\text{single molecule}} = \frac{3}{2} k_B T \quad (\text{J. per molecule})$$

The connection with our derivation above is through

$$R = k_B/m$$

where  $m$  is the mass of a single molecule, so that

$$KE_{\text{single molecule}} = \frac{3}{2} m R T \quad (\text{J. per molecule})$$

which converts to

$$KE_{\text{per cubic meter}} = \frac{3}{2} \rho R T = \frac{3}{2} p \quad (\text{J. m}^{-3})$$

as derived above (§) ; we used here the number of molecules per cubic meter,  $\rho/m$ . Notice how the small number  $k_B$  is sort of the inverse of Avogadro's big number, with both allowing us to convert from single-molecule energy to the more useful energy of one mole of gas.

*Specific heat capacity.* Molecules with two or more atoms have additional ways to store energy, beyond their KE of translation. The kinetic energy of such molecules is still responsible for pressure and hence temperature, but there are additional ways to store energy: rotation of a diatomic molecule like nitrogen, and possibly elastic vibration of the two atoms. The total stored energy of the molecule is the sum of the 3 components of KE (3 velocity components), plus 2 components due to rotation about two axes normal to the line joining the atoms (not 3, since rotation about the line joining the atoms contributes negligible energy). This means that different gases require different amounts of heating to raise their temperatures by 1 degree. Monatomic gases (like the noble gases, argon, helium....) have just the 3 components of KE, whereas diatomic gases like nitrogen and oxygen have 5 ways to store energy. However at very high temperature elastic vibrations of the two atoms are excited, giving two more degrees of freedom to diatomic molecules for a total of 7 degrees of freedom. These are classical-physics ideas and quantum mechanical structure of molecules with their orbital electrons yields more complexity.

The 1<sup>st</sup> law of thermodynamics

$$\delta E = \delta'Q - p \delta v \quad (\text{.....} = \delta'Q + (p/\rho^2) \delta \rho)$$

gives the relation between an increment of heating, say  $\delta'Q$ , and internal energy change, say  $\delta E$ .  $v$  is specific volume,  $v = 1/\rho$ . If the volume is held constant,  $\delta E = \delta'Q$  and for molecules with a fixed number of degrees of freedom

$$E = C_v T \quad (\text{J kg}^{-1})$$

where  $C_v = \delta'Q/\delta T$  is the 'specific heat capacity at constant volume,  $v$ , and  $T$  is Kelvin temperature.

For a monatomic gas  $C_v = (3/2)R$ ; for a diatomic gas there are two more degrees of freedom, and

$$C_v = (5/2)R$$

unless hot enough to awaken vibrational degrees of freedom.

If instead the atmosphere is allowed to expand upward as it is heated, keeping the hydrostatic pressure constant at each parcel of fluid, the specific heat is  $C_p = \delta'Q/\delta T$  at constant pressure. From the 1<sup>st</sup> law we find

$$C_p - C_v = R,$$

so that for air (diatomic)  $C_p = (7/2)R$ .

*Internal thermal energy and mechanical potential energy.* The heated column of atmosphere expands upward, raising its center of mass in the vertical,  $z$  direction, and hence increasing the gravitational potential energy, PE, of the air:  $PE = g \times \text{mass of air} \times \text{center of mass}$ ,  $\int g p z \, dz$ . This sharing of energy means that more heating is needed to raise the temperature by 1 degree. Without any further calculation, we find that the heat energy converted to PE is the 'left over'  $(C_p - C_v) \delta T$  and the ratio of mechanical, potential energy produced to internal, thermal energy increase  $C_v \delta T$  is

$$\frac{(C_p - C_v) \delta T}{C_v \delta T} = \gamma - 1 \quad \gamma = \frac{C_p}{C_v}$$

The ratio of specific heats  $\gamma = C_p/C_v = 7/5$  for diatomic gas. In this case heating the atmosphere produces gravitational PE which is fully 40% of the increase in thermal internal energy. This PE can convert to the KE of the circulation.

An equivalent calculation for the ocean shows very much smaller fraction of solar heating going into PE, because the thermal expansion coefficient of seawater is so much smaller than that of air. The

thermal expansion coefficient,  $\alpha = \frac{1}{\rho} \frac{\partial \rho}{\partial T}$  ( $K^{-1}$ ) at constant pressure is just  $1/T$  for air  $\sim 1/300$  at room temperature. Whereas, for warm seawater  $\alpha \approx 2 \times 10^{-4}$  ( $K^{-1}$ ) which is 0.06 times that of air.

*Climate system.* This tells us something useful about the coupled ocean/atmosphere system: the atmosphere readily converts solar heating (and heating from the oceans beneath) into mechanical energy of circulation, while the ocean is more sluggish. As well as the small thermal expansion of water, the ocean circulation is inhibited by the heating and cooling at its upper surface. It is far more efficient to heat a fluid from below or internally, as the atmosphere is. (Recall that the efficient heat engine involves heating the gas at high pressure, cooling it at low pressure.)

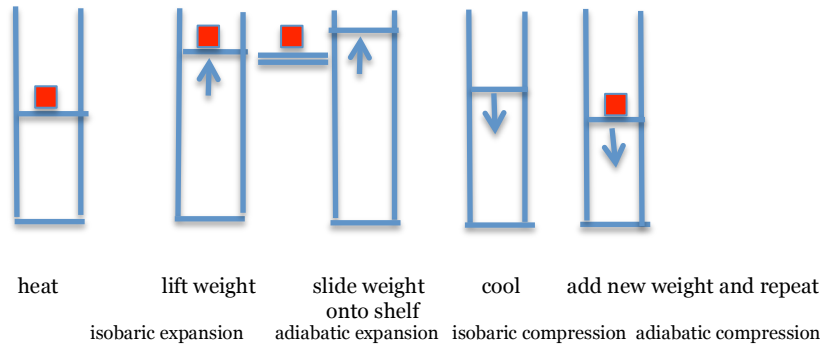
Winds in the atmosphere drive ocean circulation independent of that due to thermal forcing. There is in fact a proof (about 2 or 3 lines long) by Paperella and Young (J. Fluid Mech. 2002) showing that heating and cooling at the top of the ocean will, by itself, drive only negligibly small circulation at large scale, unless another source of energy is also present (winds or tides).

Gill's textbook has good introductory chapters with some general properties of oceans and atmosphere. First, the phase change of water is a key part of the energy balance of the atmosphere, through the transport of latent heat in water vapor. It takes about 2.5 million Joules of heating to evaporate one kg. of water at  $T = 20^\circ C$ . The oceans evaporate on average about one meter per year of water (of course more in hot, dry regions), and yet the average amount of water in the whole atmosphere above would amount to only  $\sim 2$  cm. of liquid water, if condensed. The residence time of water in the atmosphere is rather short, but south winds do carry water vapor to high latitude where it gives up its heat as it precipitates. Locally in the tropics there is also significant recycling of water and latent heat release in towering cumulus clouds and tropical cyclones. Fully  $1/2$  of the meridional transport of heat by the atmosphere from tropics to polar regions is in the form of latent heat transport (water vapor), rather than just in warm winds ('sensible heat transport'). The ocean returns this water vapor equatorward, and its overturning circulation transports heat at a rate a bit less than the atmosphere, yet still very significant.

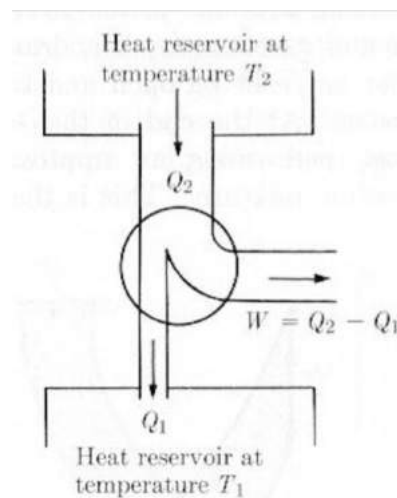
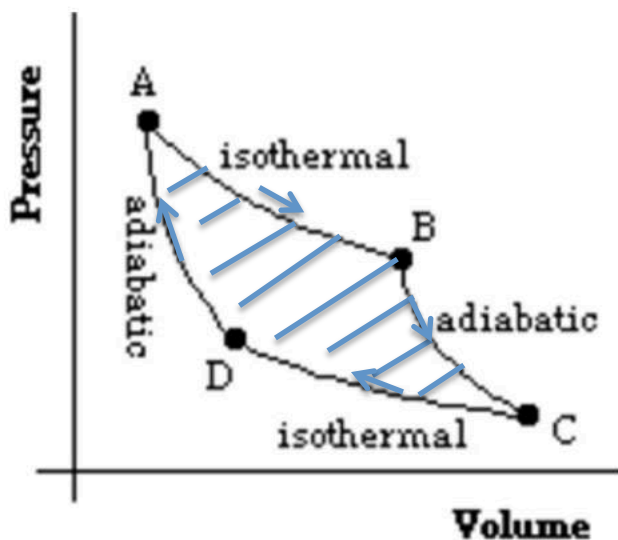
*Convection and heat engines.* We want to relate the complex process of thermal convection to a simpler mechanical model, an engine that converts heat into mechanical energy (KE or PE). The Stirling engine shown in the lab is an example. It works by heating a trapped volume of air, which expands. The air is in a glass tube that can rock back and forth like a see-saw, and is forced to do so by the motion of the row of yellow marbles. Part of the expanded air flows through a plastic tube which then exerts an upward force on the right end of the 'see-saw'. It tips down at the left; this moves the row of yellow marbles over to the site of the heating. The air is displaced by this, far from the heat source where it cools. The cooled air contracts and, communicated through that same plastic tube, allows the see-saw to rock back up at the left end, the marbles move to the right, and the air is once again close to the heat source. A short video from our GFD lab shows the thermal engine at work: [www.ocean.washington.edu/research/gfd/stirling.m4v](http://www.ocean.washington.edu/research/gfd/stirling.m4v)



It's very difficult to write about this clearly, so perhaps imagine a simple column of air with a moveable lid on top, upon which there is a red weight. Heat the air, allowing it to expand at constant pressure, lifting the lid. We can then remove the weight onto a high shelf, and we have done mechanical work, stored as PE of the weight. Relieved of its weight, the lid rises a bit farther, adiabatically (no heating or cooling). Now cool the air column back down, so that it shrinks downward. Finally place another weight on the lid. The air column compresses further, adiabatically. Once again apply heat at constant volume, allow the gas to expand lifting the mass, slide it onto the shelf, etc. This is a cyclic heat engine which appears on a plot of pressure  $P$  against volume  $V$  ( $V$  is proportional to  $1/\rho$ ).



If the air cycles round the  $P$ - $V$  plane clockwise, it does this work. The key is to heat the air at high pressure, let it expand, and cool it at low pressure. The amount of mechanical energy produced (the 'work done') is  $\oint P dV$ , calculated following the curve round one cycle. This is the area (cross-hatched in the figure) enclosed by the closed curve. With  $P$  being force/ $A$  and  $V$  being distance times  $A$ , the integral becomes the integral of force times distance, which is the basic expression for work done, or mechanical energy created. The most efficient heat engine uses the Carnot Cycle, shown in the figure, where heating at high pressure ( $A \Rightarrow B$ ) occurs at constant temperature while expansion ( $B \Rightarrow C$ ) and compression ( $D \Rightarrow A$ ) are adiabatic...no heat input. The net mechanical energy produced by this cycle is a fraction  $1 - T_C/T_A$  of the heat flow entering the system. This provides an ideal limit for the efficiency of convection in converting heating into fluid circulation (think of the two temperatures as the cold and hot extremes experienced by a fluid parcel). The righthand figure shows this schematically, with heat flowing from a hot boundary ( $T_2$ ) to a cold boundary ( $T_1$ ) with some of the heat flow diverted into  $W$ , the work or mechanical energy.



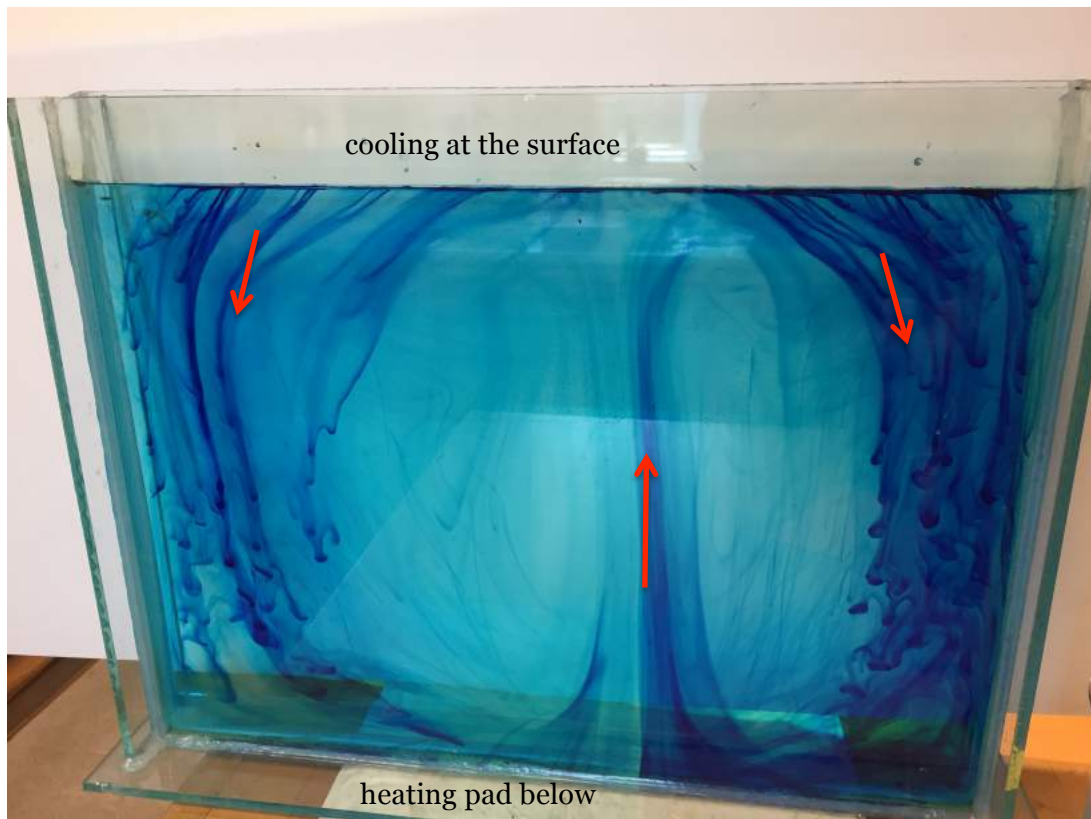
How does the P-V diagram for the example of a heated vertical air column with weight on its lid differ from this Carnot cycle? How would the mechanical energy production of these heat engines change if the working gas were helium instead of air?

The Stirling engine shares a property with most heat engines: it is a see-saw oscillator that is forced into motion by a weak buoyancy force. Car engines have flywheels, which serve the same purpose: their angular momentum helps to smooth out the impacts of exploding gasoline.

These ideas can be applied to air parcels (or water parcels) experiencing thermal convection. We looked briefly at convection with a thin cell of water heated from below. Two circulation cells developed with upward flow in the middle (image below). The life cycle of the experiment, from a cold start, is as follows. When the heat is switched on, it diffuses upward from the bottom glass boundary. The temperature obeys the diffusion equation, and hence warming reaches a distance  $d \sim (\kappa t)^{1/2}$  above the boundary where  $t$  is the time and  $\kappa$  is the thermal diffusivity ( $\text{m}^2 \text{sec}^{-1}$ ). Initially there is no fluid motion, just heat diffusion. An estimate of the buoyancy force divided by the viscous force comes from scale analysis of the heat equation (with fluid advection included). It is the Rayleigh number,

$$Ra = \frac{g \delta \rho d^3}{\kappa \nu}$$

where  $g$  is the gravity acceleration,  $\delta \rho$  is the density difference over a vertical distance  $d$ ,  $\kappa$  is thermal diffusion coefficient and  $\nu$  is kinematic viscosity (momentum diffusion coefficient). You can see that the numerator is related to buoyancy force while the terms in the denominator express viscous force and diffusive loss of buoyancy. So when  $Ra$  is large enough for upward buoyancy to overcome friction and diffusive loss of buoyancy, convection can occur ( $Ra$  has to exceed about 2000 to do so.) The term  $d^3$  is there to make  $Ra$  dimensionless. But if we identify  $d$  with the diffusion distance  $(\kappa t)^{1/2}$  we see that  $Ra$  will increase with time, and eventually buoyancy forces win out, and convection begins.





Initially the convection cells will be very small plumes of width  $\sim d$ . But rather quickly they coalesce into larger plumes, which have less diffusive damping. Soon we are left with two big cells of overturning. This cascade to large scale flow is relevant to cloud convection and to downward convection in the ocean, when its surface is cooled by the atmosphere. The great planetary cells of meridional overturning in both atmosphere and ocean are, in a sense, the ultimate convection cells, though not without important mechanical forcing as well. Fully developed convection has velocities forming a boundary layer at the bottom, where heat diffuses in from the bottom, and is swept away by the strong flow. The sinking branch tends to keep the boundary layer thin.

Nature finds ways to increase the transports of interesting quantities in fluids. Here, convection carries heat upward much more strongly than pure diffusion would, if there were no fluid motion. We can estimate the heat flux at the base as  $\kappa \partial T / \partial z \sim \kappa \Delta T / h$  where  $h$  is the boundary layer thickness and  $\Delta T$  is the top-to-bottom temperature difference. Simple diffusion without circulation would have upward heat flux  $\kappa \Delta T / H$  where  $H$  is the total height of the fluid. Thus the ratio of heat flux by convection to that by simple heat diffusion without flow is simply  $H/h \gg 1$ . This amplification of heat flux by circulation is so useful that it has a name: the Nusselt number.

*Phase change: steam engines.* Finally, we looked at a boat propelled by a steam engine, with no moving parts. Evaporation of water absorbs a huge amount of heat, which is turned back into sensible heat where condensation back to liquid occurs.  $2.25 \times 10^6$  Joules per kg. of water evaporated (boiled), at  $100^\circ\text{C}$ . The changes in pressure and volume are very great, hence the work done. The 'pop-pop' boat has a chamber attached to 2 pipes that lead out into the water at the stern. A candle beneath the chamber boils the water in it, which is thrust out one of the pipes, sucking new, cold water into the chamber through the other pipe. The momentum of the outflow propels the boat forward. The image at the right is a homemade version with a coil of metal tubing above the candle, rather than a single chamber.



A home-made pop pop boat using a coil type boiler