Lecture 9: First law and Reversibility

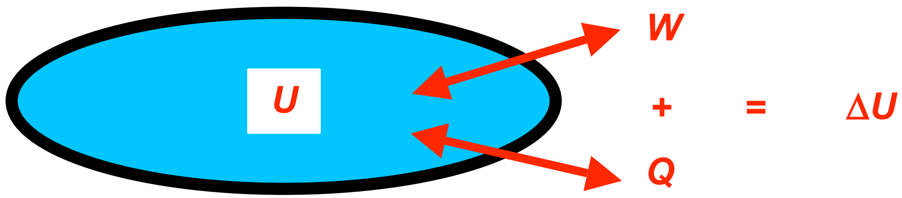
- The first law of thermodynamics
- Van Ness' article on the 1st law
- Adam's key points on the Van Ness article
- Reversibility
- Reversible processes are special
- Further reading

The first law of thermodynamics

- The first law of thermodynamics is usually written as:

$$dU = Q + W \quad \textbf{(9.1)}$$

where dU is the change in internal energy, Q is the heat and W is the work done. It is really just the conservation of energy – any change in the internal energy of a system is due to either heat passing to or from the system or work done by or on the system.



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van Ness' article on the First law

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- I'm giving you each a copy of a section of Van Ness' book "Understanding Thermodynamics" on the first law of thermodynamics – it will appear on the website after the lecture too. This is probably the best discussion of the 1st law that I've ever seen and I certainly can't out do it.

- I'll let you read it in your own time, but some comments on the main points...

1

Energy Conservation— The First Law of Thermodynamics

What is thermodynamics? Very briefly, it is the study of energy and its transformations. We can also say immediately that all of thermodynamics is contained implicitly within two apparently simple statements called *the First and Second Laws of Thermodynamics*. If you know anything about these laws, you know that they have to do with energy—the first, explicitly, and the second, implicitly. The First Law says that energy is conserved. That's all; you don't get something for nothing. The Second Law says that even within the framework of conservation, you can't have it just *any* way you might like it. If you think things are going to be perfect, forget it. The Second Law invokes

Adam's key points on the van Ness article

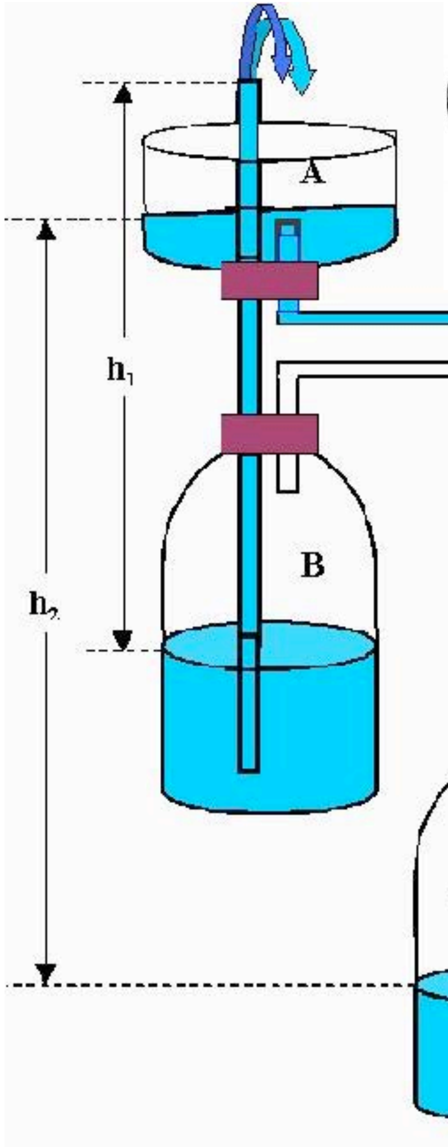
- **I now see why I was so confused about the signs in the first law – is it *dU* = *Q* + *W* or *dU* = *Q* – *W* or what? Every time I saw it, the signs were different – such that by the time I was done with my studies I'd seen all four versions and I was really confused. It all just depends on which way you see the energy going in or out of the system.**

  It all depends on which way you see the energy going. The most frequent version in older books is *dU* = *Q* – *W* because when people dealt with heat engines, they cared about heat in and work out. In most modern texts, its *dU* = *Q* + *W*, such that there is a sensible convention of + being energy entering the system (it gains internal energy) and – being energy leaving the system (it loses internal energy).

- **The first law really just a counting system, and so it's as fundamental as 1 + 1 = 2. It's interesting to realise that the first law can't be derived, and that's probably why very little gets taught about it, you can't write a 'nice string of algebra' to show how it's obtained from first principles – it's a blind observation about how the world works.**

- **The first law doesn't just have to be *dU* = *Q* + *W*, you can add or remove energy terms as you require. This is kind of nice, the physics becomes like a lego kit, you just adapt it to how you need it. The only reason only *Q* and *W* are in there is that those were the two terms most important to the steam engines guys of the 1800s!**

Hero's Fountain



Hero of Alexandria discovered this in around 50AD, Where does the energy come from???

Thus, the pressure of the water in the fountain is the difference of the hydrostatic pressures in the vessels *C* and *B*. Therefore

$$\Delta P = P_2 - P_1 = \rho g h_2 - \rho g h_1 = \rho g (h_2 - h_1). \qquad (1)$$

In other words the pressure ΔP compresses the air in the upper vessel *B* and drives the fountain.

The potential energy of a unit volume of water on the level of the reservoir *A* and the nozzle are respectively $\rho g h_2$ and $\rho g h_1$, and kinetic energies are respectively zero and $\frac{\rho v^2}{2}$. Thus we have from Bernoulli's equation

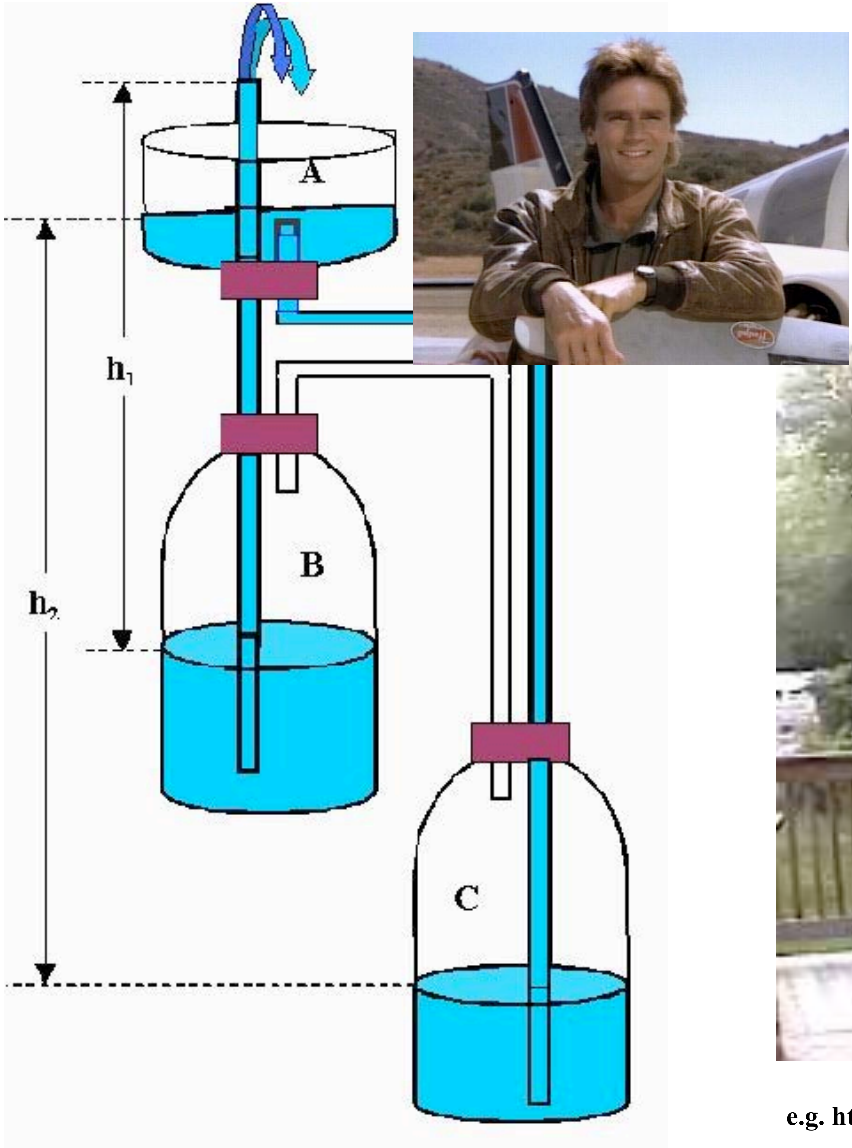
$$P_{atm} + \frac{\rho v^2}{2} + \rho g h_1 = P_{atm} + \rho g h_2\,, \qquad (2)$$

where P_{atm} is atmospheric pressure. The speed of the stream of water from the nozzle of the fountain tube can be found easily from equations (2) and (1) as

$$v = \sqrt{2g(h_2 - h_1)} = \sqrt{\frac{2\Delta P}{\rho}}. \qquad (3)$$

Hero’s Fountain

Hero's Fountain



Build one yourself…

e.g. http://www.rose-hulman.edu/~moloney/AppComp/2001Entries/e09k/fountain.htm

1^{st} law – Practice exam question

a) **There are two idealised ways of compressing a gas. The first is isothermal compression, which is so slow that the temperature of the gas doesn't rise at all. The second is adiabatic, which is so fast that no heat escapes from the gas during the process. For a monatomic ideal gas, the internal energy $U = 3/2\ Nk_BT$.**

For an isothermal compression, show that $Q = Nk_BT \ln (V_f/V_i)$. Given that $V_f < V_i$, what is the sign of Q? Does heat enter or leave the system in an isothermal compression?

for an isothermal process

$$W = -\int P.dV$$
$$= -\int \frac{nRT}{V} dV.$$
$$= -nRT\left[\ln V\right]_{V_i}^{V_f}$$
$$= -nRT(\ln V_f - \ln V_i)$$
$$= -nRT \ln(V_f/V_i)$$

Now $dU = Q + W$ but since $U = {}^3/_2 Nk_BT$ and the process is isothermal then T is a constant, so U is a constant and

$dU = 0 \Rightarrow Q + W = 0$, $Q = -W = nRT \ln(V_f/V_i)$

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Because its a compression $V_F < V_i$ ∴ $V_F/V_i < 1$ so $\ln \frac{V_F}{V_i} < 0$ so $W > 0$ and so we do work on the system to compress it. This would increase the internal energy of the system, but since $dU = 0$, this means heat must leave the system which makes sense as $W > 0$, $Q = -W$ ∴ $Q < 0$ is negative.

1st law – Practice exam question

b) **Using the first law, the expression for *U* given above and *dW* = –*PdV*, show that for the adiabatic compression of an ideal gas:**

$$\frac{3}{2}\frac{dT}{T} = -\frac{dV}{V}$$

(Hint: Do not use PV^{γ} = const, you'll show that in part (c) and don't integrate *dW* to get *W* like in (a)).

In the adiabatic case $Q = 0$ so $dU = W$.

Now $U = \frac{3}{2} N k_B T$ and so $\frac{dU}{dT} = \frac{3}{2} N k_B$

$\Rightarrow dU = \frac{3}{2} N k_B \, dT$

also $dW = -P dV$, so for a very small compression

$dU = dW$

$\frac{3}{2} N k_B \, dT = -P dV$ using $P = \frac{N k_B T}{V}$

$= -\frac{N k_B T}{V} dV$.

$\frac{3}{2}\frac{dT}{T} = \frac{-dV}{V}$ as required

1st law – Practice exam question

c) Integrating both sides of your result in (b) from the initial values (V_i and T_i) to the final values (V_f and T_f), and using the ideal gas law to eliminate T, show that you can obtain the relationship PV^γ = constant for an adiabatic process, where $\gamma = 5/3$.

$$\frac{3}{2}\int_{T_i}^{T_F} \frac{dT}{T} = -\int_{V_i}^{V_F} \frac{dV}{V}$$

$$\frac{3}{2}\Big[\ln T\Big]_{T_i}^{T_F} = -\Big[\ln V\Big]_{V_i}^{V_F}$$

$$\frac{3}{2}\ln\left(\frac{T_F}{T_i}\right) = -\ln\left(\frac{V_F}{V_i}\right)$$

$$\ln\left(\frac{T_F^{3/2}}{T_i^{3/2}}\right) = \ln\left(\frac{V_i}{V_F}\right)$$

take exponent of both sides

$$\frac{T_F^{3/2}}{T_i^{3/2}} = \frac{V_i}{V_F}$$

1st law – Practice exam question

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cross multiply $V_F T_F^{3/2} = V_i T_i^{3/2}$

or $V T^{3/2} = \text{Const.}$

now we use the ideal gas law to eliminate $T \Rightarrow T = \frac{PV}{nR}$.

$$V\left(\frac{PV}{nR}\right)^{3/2} = \text{Const}$$

$$V P^{3/2} V^{3/2} = (nR)^{3/2}\,\text{Const.}$$

$$P^{3/2} V^{5/2} = (nR)^{3/2}\,\text{Const.}$$

take both sides to the power of 2/3

$$\left(P^{3/2} V^{5/2}\right)^{2/3} = \left((nR)^{3/2}\,\text{Const}\right)^{2/3}$$

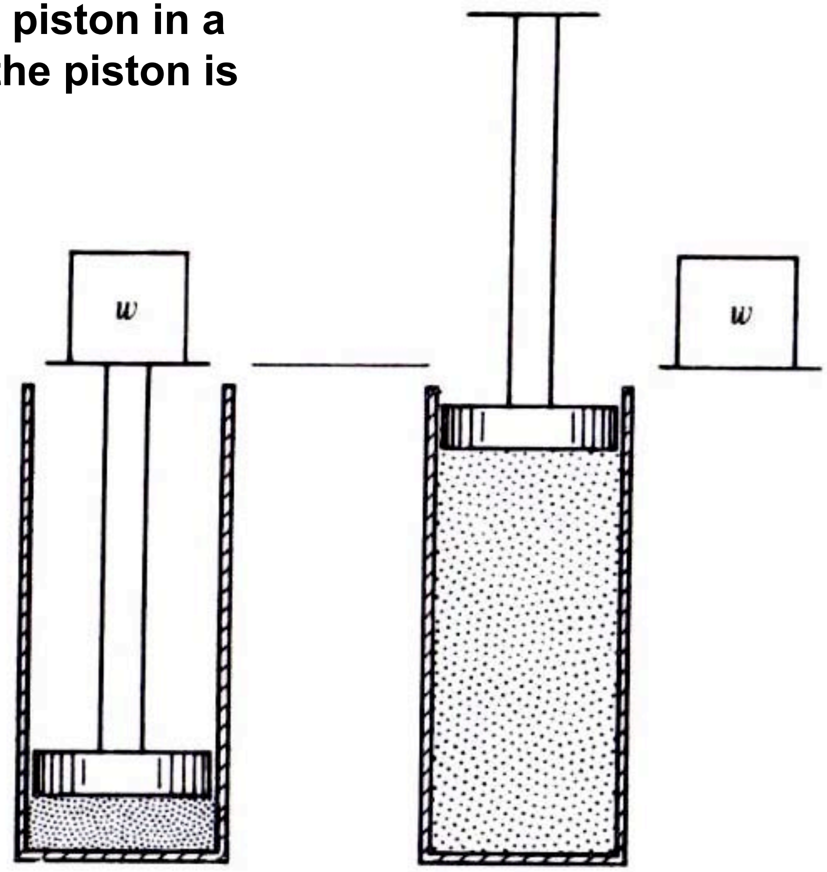
$$PV^{5/3} = \text{const} \quad \text{as required}$$

Reversibility

- I don’t want to waste a whole lecture on the first law, so I’ll stop there and change topics. I’m now going to talk about a concept that is important for our lectures on the second law and entropy – reversibility.

- Let’s start our discussion with our friendly old piston in a cylinder again, as shown below, but this time the piston is upright and has some mass *m* on top of it.

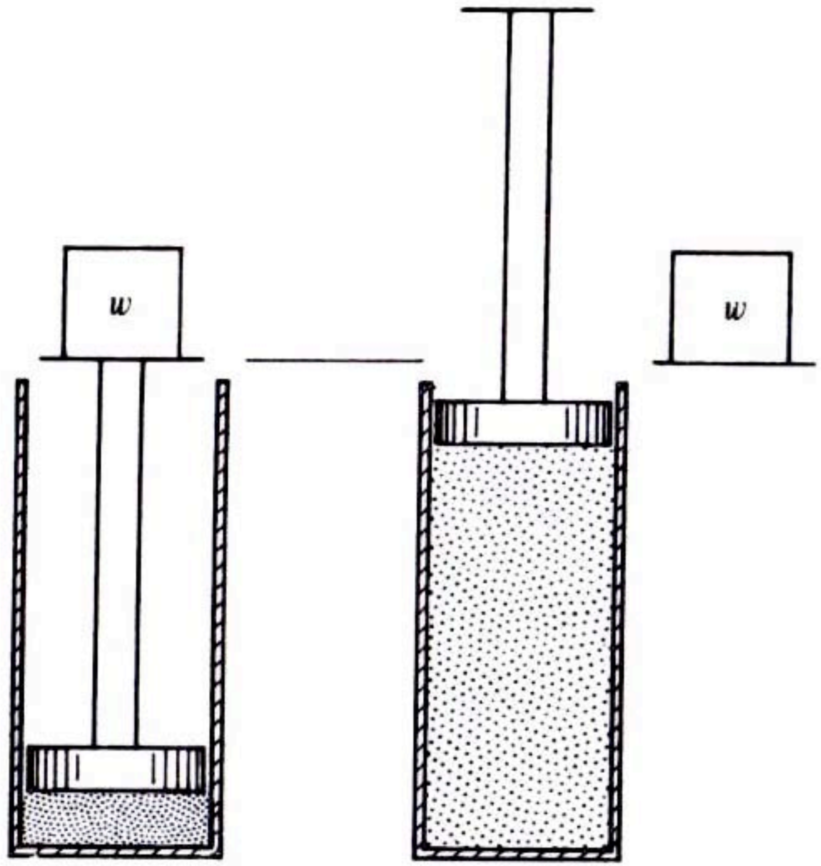
We will assume that the cylinder will is frictionless and sufficiently well insulated that any process we perform is adiabatic. What we’re interested in here is how much useful work can we get out of the piston, in other words by lifting some weight *w* on the piston (we will ignore the mass of the piston itself here, sure some work will be done by the gas in lifting it, but this is useless to us).



One big chunk

- OK, so lets start with our weight *w* on the piston in one big chunk. The piston is at equilibrium and nothing will happen until we remove or change the mass. But because its one big chunk, it's either on or off. Suppose we quickly push the mass off the piston onto a platform, what will happen?

  The piston will shoot upward and after bouncing up and down a bit, will settle into a final equilibrium position. Has it done any useful work? Well no, the mass hasn't been displaced against the next external force (i.e., gravity) and so the useful work is zero – not terribly useful to us at all.

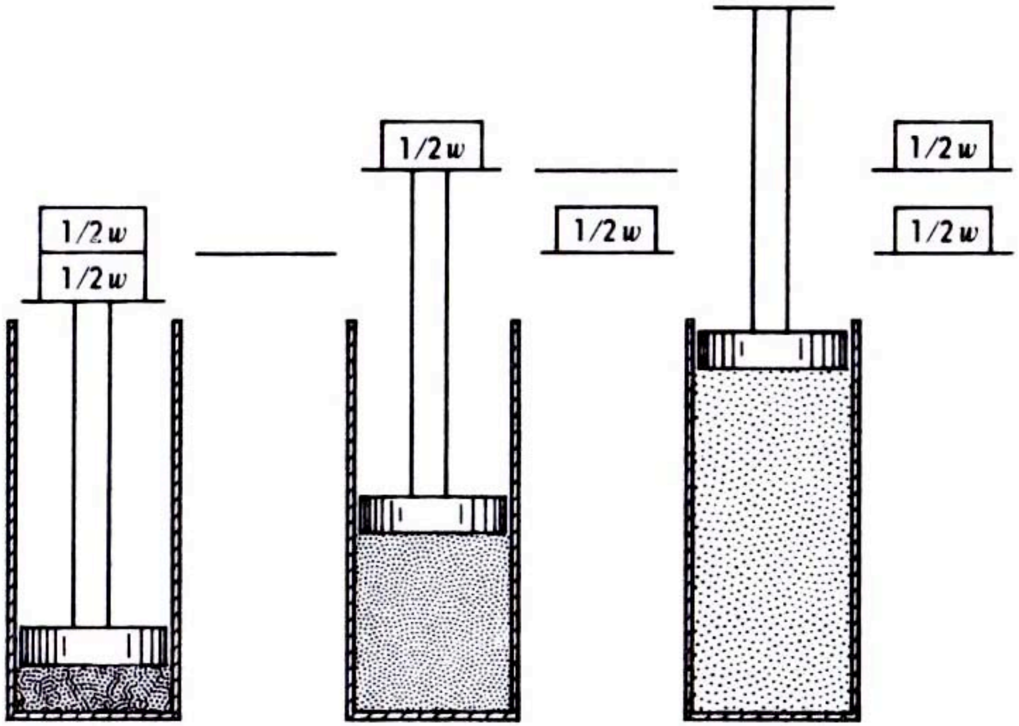


- Let's get smart here then, can anyone come up with some way to get some useful work out of this system without adding or removing anything to/from the set-up?

Cutting it in half

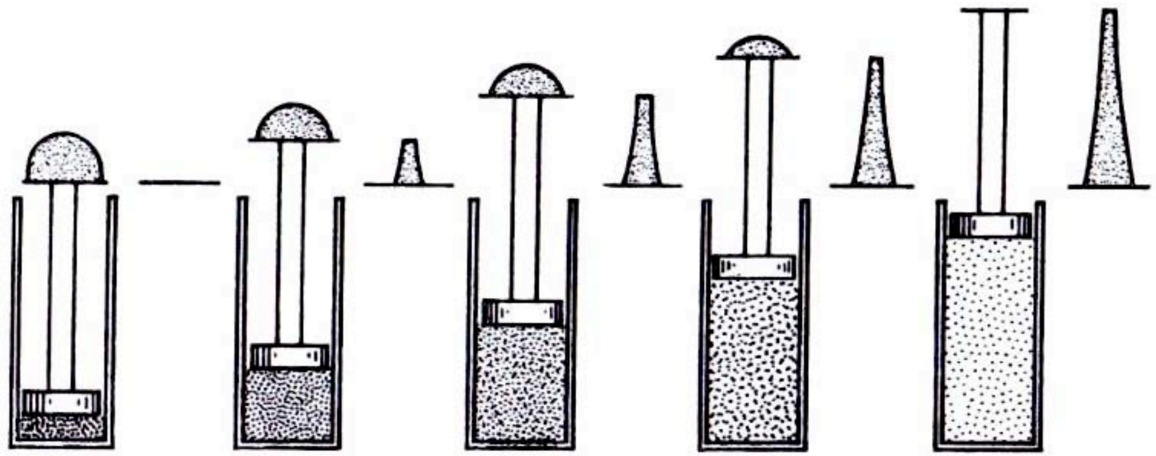
- **The crafty thing to do here is cut the weight *w* in half, so we have two weights *w*/2, as shown below. Then we can first push *w*/2 off onto a platform, the piston will then rise halfway with the other *w*/2 on it, if we then push the second *w*/2 onto a platform, the piston rises the rest of the way up to the final equilibrium state.**

  Have we done any better? Yes, we've now lifted *w*/2 half of the travel of the piston (suppose the travel is *x*, this is *x*/2) and we get an amount of useful work $W = w/2 \times x/2 = wx/4$.



Infinitesimal pieces

- So now if we're really smart, we'll take our weight *w* and grind it up into a powder containing a massive number of infinitesimal pieces d*w*, as shown below.



Now we can flick our little pieces *dw* off one by one, and each time our piston will rise by *dx* and carrying our remaining mass *w* – *ndw* with it. You guys can do the maths here if you want, but we've now lifted all of the mass by some amount, and on average by half the stroke of the piston, so we'd be somewhere around $W = wx/2$.

We call this process ***reversible*** (in the limit $dw \rightarrow 0$) because we could put the little piece *dw* that we just took off back on again, and the one before it and so on, without having to put any additional work on the system. In the earlier cases we can't do this – there's no way we can get the piston back down to where we can slide the masses *w* or *w*/2 back onto the piston without expending some external energy on the system.

Reversible processes are special

- **The reversible process is unique and holds a special place in thermodynamics because it represents the ultimate for what is possible in the real world. As an added advantage, the mathematics for reversible processes is far easier than for irreversible ones, because the forces are always almost at balance and the system never gets very far from an equilibrium state at any time.**

For example, for a reversible process we can always say that *F* = *PA* and *dV* = *Adx* and calculate the work done by:

$$W = -\int F.dx = -\int PA.\frac{dV}{A} = -\int PdV \qquad \textbf{(9.2)}$$

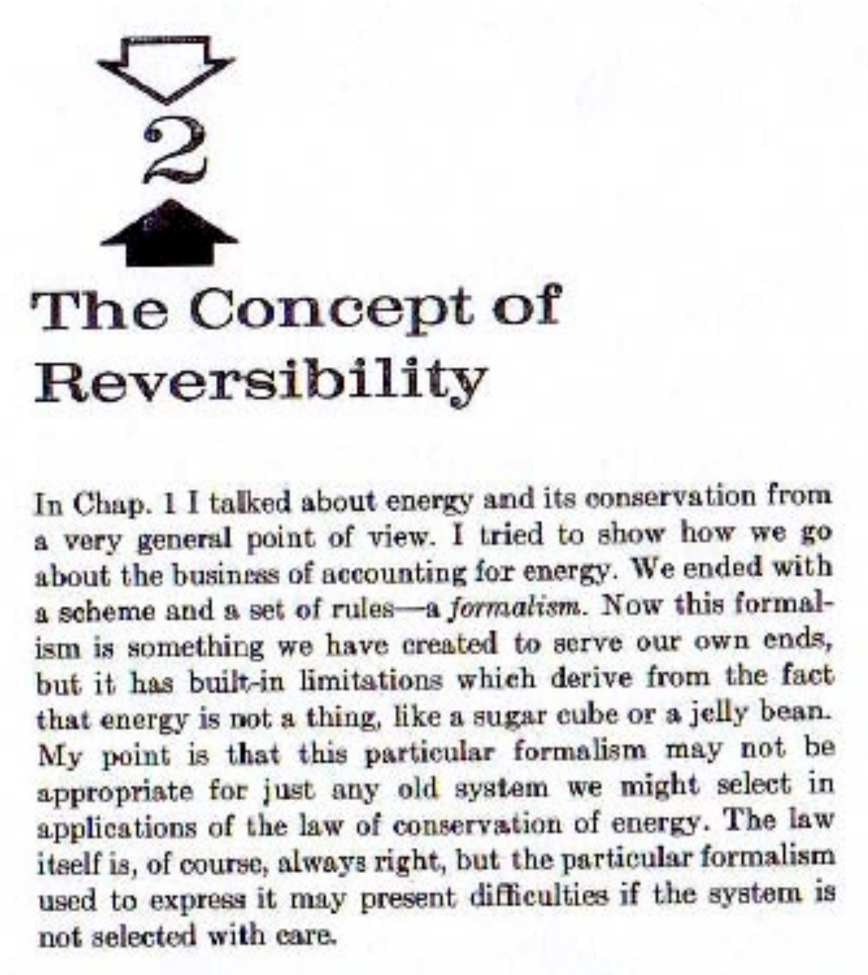
In the irreversible case this isn't true – when a finite weight is removed from the piston, the gravity acting downward is overbalanced by the gas pushing upward by some finite amount, the piston launches upward, and then damps out to its new equilibrium (bouncing up and down on the way).

In this case, *F* doesn't equal *PA* at any point except at the beginning and when the final equilibrium is reached. So we can't just substitute this into Eqn. 9-2, and things become hard to analyse.

Further reading

- **More importantly though, the useful work we get in a reversible process is the maximum possible, and because this is usually what we want, this is why we're so interested in reversible processes.**

For a more in-depth discussion, I highly recommend reading Van Ness' chapter on reversibility, which I will post on the website as additional reading.



2

The Concept of Reversibility

In Chap. 1 I talked about energy and its conservation from a very general point of view. I tried to show how we go about the business of accounting for energy. We ended with a scheme and a set of rules—a *formalism*. Now this formalism is something we have created to serve our own ends, but it has built-in limitations which derive from the fact that energy is not a thing, like a sugar cube or a jelly bean. My point is that this particular formalism may not be appropriate for just any old system we might select in applications of the law of conservation of energy. The law itself is, of course, always right, but the particular formalism used to express it may present difficulties if the system is not selected with care.

Summary

- The first law of thermodynamics is usually written as *dU* = *Q* + *W*, where *dU* is the change in internal energy, *Q* is the heat and *W* is the work done. It is really just the conservation of energy – any change in the internal energy of a system is due to either heat passing to or from the system or work done by or on the system.

- The sign convention you see in the first law depends on which way you see the energy going in or out of the system.

- The most frequent version in older books is *dU* = *Q* – *W* because they cared about heat in and work out. In most modern texts, it's commonly seen as *dU* = *Q* + *W*, such that + means energy coming into the system (it gains internal energy) and – means energy going out of the system (it loses internal energy).

- The concept of reversibility holds a unique place in thermodynamics, because it represents the ultimate for what is possible in the real world, we can't even imagine anything better. As an added advantage, the mathematics for reversible processes is far easier than for irreversible processes.

In the next lecture we will start looking at heat engines and how to calculate the efficiency of those engines, we will do this with a very common example – the internal combustion engine.