

## Chapter 34

# 34 First Law and Work

### 2.3.2, 2.3.3

We have studied the zeroth law of thermodynamics. Zero is an odd place to start numbering (unless you are programming a computer in python or C++). That no energy is transferred between to objects in thermodynamic equilibrium is so obvious that for a while it went unstated. But now we recognize from our kinetic theory of gasses why this must be the case and we can label this fact a law of thermodynamics. But there is more than one law of thermodynamics (other wise, why would we number them at all?). Let's learn another law of thermodynamics, which has to do with conservation of energy in thermodynamic systems.

### Fundamental Concepts

- The first law of Thermodynamics is just conservation of energy
- $\Delta E_{int}$  is an invariant quantity in thermodynamics
- Work in thermodynamic processes can be described as the integral  $w_{int} = \int_{V_i}^{V_f} P dV$
- $\Delta E_{int} = Q + w_{int}$  is the first law of thermodynamics

### 34.1 Conservation of Energy: First Law of Thermodynamics

Remember when we studied energy in PH 121. We used the work energy theorem

$$\Delta K = w$$

and expanded the work side to show the different types of work explicitly. We have work done by conservative forces  $w_c$  and work done by non-conservative forces (dissipative forces like friction)  $w_{nc}$ .

$$\Delta K = w_c + w_{nc}$$

and we could further divide up the work by categorizing the source of the work, say, work done by the force of gravity,  $w_g$ , or work done by a spring force  $w_s$ .

$$\Delta K = w_g + w_s + w_{nc}$$

and we could go on in more complicated systems listing all the different kinds of work.

We relabeled these different types of work as potential energies. For example,

$$\begin{aligned}\Delta U_g &= -w_g \\ \Delta U_s &= -w_s\end{aligned}$$

and rewrote the work energy theorem

$$\Delta K + \Delta U_g + \Delta U_s = w_{nc}$$

This gave us a way to think of mechanical energy in a system. But we realize that we have not covered all types of energy yet. Suppose we consider your car. You put gas in the car. This is a source of energy, a *chemical potential energy*,  $U_{chem}$ . So we should really include it.

$$\Delta K + \Delta U_g + \Delta U_s + \Delta U_{chem} = w_{nc}$$

and if your car is a DeLorean that has been modified to use nuclear energy to run, then you might have a nuclear potential energy

$$\Delta K + \Delta U_g + \Delta U_s + \Delta U_{chem} + \Delta U_{nuclear} = w_{nc}$$

and back in PH121 we called the non-conservative work  $w_{nc} = \Delta E_{th}$  because friction like forces dissipate mechanical energy by turning them into thermal energy. Then

$$\Delta K + \Delta U_g + \Delta U_s + \Delta U_{chem} + \Delta U_{nuclear} = \Delta E_{th}$$

The quantities  $\Delta U_{chem}$ ,  $\Delta U_{nuclear}$ , and  $\Delta E_{th}$  are different than the mechanical energies we studied before. They have to do with the internal workings of the material, itself. We will call an amount of energy that comes from the material, itself *internal energy*. If we think about it, we might expect that temperature has something to do with an internal energy of the object. And we would be right.

### 34.1.1 Work and Internal energy

Our potential energy terms are all derived from work. Long ago we found that the work done on an object may depend on the path the object takes. We found work using

$$w = \int_{x_i}^{x_f} \vec{F} \cdot \vec{dr} \quad (34.1)$$

and the work was the area under the force vs. displacement curve. But this was work done moving an object as a whole. Now we can do work on an object by compressing it, for example. This is different from moving the whole object around. Let's call this new kind of work *internal work*. This new kind of work should be similar in form to regular mechanical work. We expect it to depend on the details of how the internal work is done.

For mechanical work we defined the potential energy,  $U$ , as

$$w = -\Delta U \quad (34.2)$$

Using this concept, we showed that mechanical energy

$$E_{mech} = K + U \quad (34.3)$$

was often conserved, when  $E_{thermal} = 0$  where  $E_{mech}$  was the total mechanic energy. Remember we solved a lot of problems back in Principles of Physics I by knowing that for a closed system,  $E_{mech}$  did not change. In other words,  $E_{mech}$  was independent of path we take on our  $F$  vs.  $x$  diagram. This makes  $E_{mech}$  much easier to work with. A path independent quantity makes problems easier.

We want another variable to work with that removes the difficulty of worrying about the details of how the internal motion happens (the path). But we can't use the kinetic energy for this. The kinetic energy is part of the mechanical work of the object as a whole, and does not affect the internal workings of the object.

Frictional forces do affect the object. Think of rubbing your hands together. There is mechanical work done by your muscles. There is kinetic energy while your hands move. But your hands heat up. This higher temperature is still there for a while after your hands stop moving. Eventually the temperature of your hands returns to normal. We now know to call this transfer of energy heat,  $Q$ .

Now that we remember all of this, we are ready to find our path independent quantity for internal energy. We define the change in internal energy as

$$\Delta E_{int} = Q + w_{int}$$

As with the mechanical energy, the change in internal energy does not depend on the details of how the change happens (what we are calling the "path"). The change in energy is used because  $Q$  and  $w$  are transfer variables, so they *do* depend on the details of the transfer. For small changes we can write

$$\Delta E_{int} = \Delta Q + \Delta w_{int}$$

or for very small changes, we could replace the  $\Delta$ 's with small  $d$ 's

$$dE_{int} = dQ + dw_{int}$$

but be careful! these are not true differentials because  $dw$  depends on the path! Integration of  $dw$  is trick and you would have to think about it carefully. The relationship

$$\Delta E_{int} = Q + w_{int} \quad (34.4)$$

is known as the *first law of thermodynamics*.

Let's look at some systems and think about their internal energies.

### 34.1.2 An Isolated System

Last lecture we defined isolated systems. An isolated system is a system separated from the rest of the universe. Nothing can act on it. When a system is isolated, we have

$$w_{int} = 0 \quad (34.5)$$

because no work can be done on an isolated system and

$$Q = 0 \quad (34.6)$$

because no heat can flow to or from an isolated system so

$$\Delta E_{int} = w_{int} + Q = 0 \quad (34.7)$$

### 34.1.3 A Cyclic Process

Suppose we have a process, something that is done to a sample of matter, say a gas, over and over again the say way. We call such a process a *cyclic* process. This is like the pistons in your car going through the same motion over and over again to compress the gas in your engine cylinders. Let's practice with the idea of internal energy, work, heat and PV diagrams for such a process. If a process repeats, it starts and ends in the same state so then

$$\Delta E_{int} = 0 \quad (34.8)$$

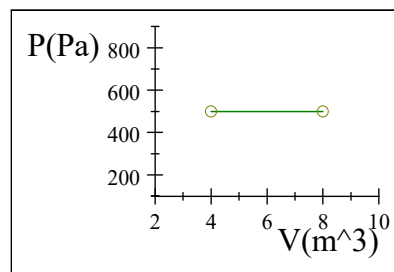
and

$$Q = -w_{int} \quad (34.9)$$

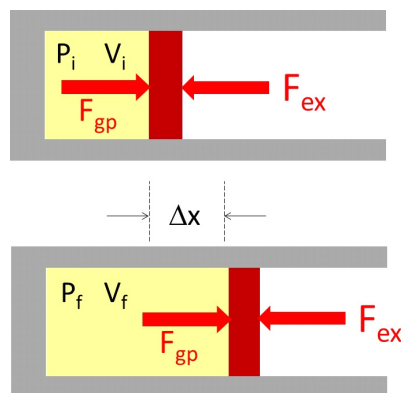
But these examples were too easy. Let's take on a harder problem where we actually find the amount of work done.

## 34.2 Work

- Consider the work done by a piston as it compresses a gas. It might be good if the amount of work was equal to the amount of energy transfer by heat. We often want this to be true! Otherwise you could melt your engine as your car operates. We want an engine in a car (or train, or airplane) to be a cyclic process. This explains why your car engine surface gets hot. Work is being done in the cylinders in your engine, but to make the process cyclic some energy must be lost by heat or the energy would rise. Unlike your car pistons, let's do this slowly and quazi-statically so that the pressure equalizes every time we move the piston a little bit.



Then the pressure won't change. Let's call such a process where the pressure doesn't change in the cylinder an *isobaric process*.<sup>1</sup>



Lets take a close look at the gas within the piston. At equilibrium we know

$$P = \frac{F_P}{A}$$

or

$$F_P = PA$$

<sup>1</sup>There are details of car engines that we won't tackle until later. So not everything in this lecture applies directly to car engines.

This force is the force of the gas pushing on the piston. We could label it

$$F_{gp} = F_P$$

Notice that the gas pushes to the right. If we apply an external force to the piston slowly so as to allow the system to remain in thermal equilibrium as we go, then

$$\vec{F}_{ex} = -F_{ex}\hat{x}$$

because we are pushing in the  $-x$ -direction. Again, we will move the piston slowly so we don't violate our quasi-static rule. As we move the piston the gas inside the piston adjusts in pressure until we are again in equilibrium. So

$$F_{ex} = F_{gp}$$

but the pressure force  $F_{gp}$  pushes the opposite direction

$$\begin{aligned}\vec{F}_{gp} &= +F_{ex}\hat{x} \\ &= PA\hat{x}\end{aligned}$$

We should also note that since neither the piston nor the gas are accelerating, Newton's third law tells us that the force of the gas on the piston and the force of the piston on the gas are equal in magnitude but opposite in direction

$$\begin{aligned}F_{gp} &= F_{pg} \\ \vec{F}_{gp} &= -F_{pg}\hat{x}\end{aligned}$$

When we move the piston to the left, we have a displacement

$$\vec{dr} = -dx\hat{x}$$

so the work done *on the gas by the piston* would be

$$w_{gp} = \int_{x_i}^{x_f} \vec{F}_{ex} \cdot d\vec{r}$$

Remembering how to use a dot product we can write this as

$$w_{gp} = \int_{x_i}^{x_f} F_{ex} dx \cos \theta_{Fx}$$

It is worth remembering that in this formula  $F_{ex}$  and  $dx$  are magnitudes. Let's write this as

$$w_{gp} = \int_{x_i}^{x_f} |F_{ex}| |dx| \cos \theta_{Fx}$$

to remind us. Substituting in  $|F_{gp}|$  for  $|F_{ex}|$  (since they have the same magnitude) we have

$$\begin{aligned}w_{gp} &= \int_{x_i}^{x_f} |F_{gp}| |dx| \cos \theta_{Fx} \\ &= \int_{x_i}^{x_f} |PA| |dx| \cos \theta_{Fx}\end{aligned}$$

and the angle between  $F_{ex}$  and  $dx$  is  $180^\circ$ . If this seems mysterious, look at the last figure, and remember we are really working with  $F_{ex}$ . We put in  $F_{pg}$  because it's magnitude is the same as that of  $F_{ex}$ . So  $180^\circ$  is the right angle for our dot product.

$$w_{gp} = - \int_{x_i}^{x_f} |PA| |dx|$$

To get the total work done on the piston we are integrating over the entire path of the piston travels. It is worth noting that  $P$  can only be positive, and the same is true for  $A$ . Both  $P$  and  $A$  are constant, since we are using our quasi-static process and allowing the pressure to equalize as we go. So we could write the work done on the piston by the gas as

$$w_{gp} = PA \int_{x_i}^{x_f} |dx|$$

but now we need to consider  $|dx|$ . We know that  $dx$  is a small displacement, and displacements can be negative. And in our case, as the piston goes to the left,  $dx$  certainly is negative. But no matter, we don't just have  $dx$ , we have  $|dx|$ . But there is a problem. We got a minus sign from our dot product, but we would like the work done by the piston on the gas to be a positive number. And it looks like our integral will be negative.

But here we can be a little bit clever. If  $dx$  really is negative, then the negative hiding inside of  $dx$  cancels the negative sign from our dot product. And then

$$w_{gp} = -PA \int_{x_i}^{x_f} dx$$

still gives us positive work (think of what we did with springs in PH121 to deal with  $S = -k(x - x_o)$  in work integrals). Now we don't have to worry about integrating with absolute value signs.

Remember that we are using an isobaric process in compressing the gas. That is, we keep the pressure the same but allow the temperature to change, so that the volume and temperature change proportionally  $V = (nRT/P)$ . So our integral is just

$$\begin{aligned} w_{gp} &= -PA \int_{x_i}^{x_f} dx \\ &= -PA(x_f - x_i) \end{aligned}$$

We can rewrite this result using what we know about the volume of the gas

$$V = A\Delta x$$

so the work done by the gas pushing on the piston is

$$\begin{aligned} w_{gp} &= -P(Ax_f - Ax_i) \\ &= -P(V_f - V_i) \end{aligned}$$

This gives us an idea. We could write the quantity  $Adx$  as  $dV$  and change the limits of integration from  $x_f$  and  $x_i$  to  $V_f$  and  $V_i$ . Then our integral would be

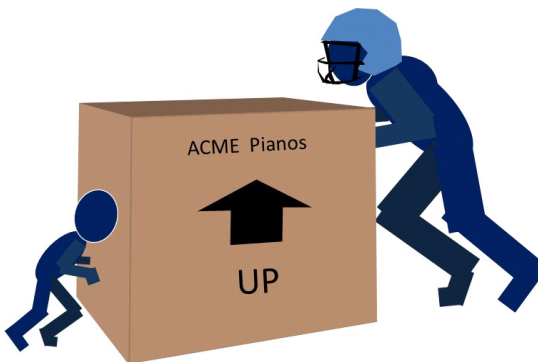
$$\begin{aligned} w_{gp} &= - \int_{x_i}^{x_f} PAdx \\ &= - \int_{V_i}^{V_f} PdV \end{aligned}$$

This gives the same answer for the work done on the piston for our isobaric case

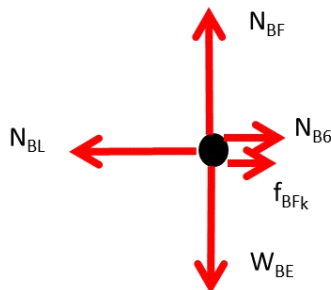
$$w_{gp} = -P(V_f - V_i)$$

But this is the amount of work that the piston does on the gas. Is the gas pushing back on the piston? Of course it is! And that push is also a force,  $F_{pg}$ , so it also does work. But let's review what we know about work from PH121.

Suppose we have two people exerting a force on a box. One is a professional American football player, The other is a six-year-old.



They push in opposite directions. How much work is being done? To answer this, let's consider a free-body diagram.



where the subscript  $B$  is for the box and the subscript 6 is for the six-year-old



and  $L$  is for the football player (In this case, a (L)inebacker). We can see that there will be a net force.

$$F_{net_s} = N_{BL} - N_{B6} - f_{BF}$$

But which way will the box go? We could guess that the football player will push the box *and* the six-year-old to the left. So  $\Delta s$  will be negative. Then the work done on the box by the football player will be

$$\begin{aligned} w_{BL} &= \int_{s_i}^{s_f} N_{BL} ds \\ &= N_{BL} \Delta s \end{aligned}$$

but the work done by the child would be

$$\begin{aligned} w_{B6} &= \int_{s_i}^{s_f} -N_{B6} ds \\ &= -N_{BM} \Delta s \end{aligned}$$

The child's work is negative! What can that mean? Well, for starters, the child's force can't be the force that is making the box move. In fact, the child's force is another obstacle that the linebacker's force must overcome to make the box move. This means that the linebacker must do enough work (push hard enough) to make the box go, *and* to overcome the backward push of the child.

But that is just our case with the gas and piston. The gas pressure force *is* pushing on the piston. But the gas pressure force on the piston is losing ground (the external force is pushing the piston to the left). So we would expect the work done by the gas on the piston to be negative.

Since we assumed a quasi-static process, the two forces must always be nearly the same,

$$|F_{ex}| = |F_{pg}|$$

so the amount of work must be nearly the same, but the sign must be negative for the work on the gas due to the piston's push. We wrote the work done by the piston on the gas as

$$w_{gp} = - \int_{V_i}^{V_f} P dV$$

Then the work done by the gas on the piston must be

$$\begin{aligned} w_{pg} &= - \left( - \int_{V_i}^{V_f} P dV \right) \\ &= \int_{V_i}^{V_f} P dV \end{aligned}$$

that is, the work done on the gas by the piston is the negative of the work done on the piston by the gas.

We are principally interested in what happens to the gas, (we studied objects like the piston in Principles of Physics I) so the first equation is what we are looking for. This is the internal work done on the gas!

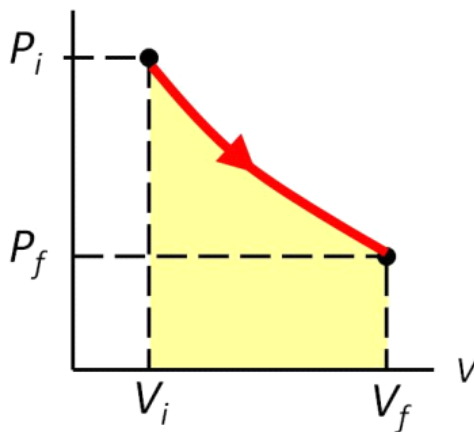
$$w_{gp} = w_{\text{on the gas}} = w_{int} = - \int_{V_i}^{V_f} P dV \quad (34.10)$$

And we could also define

$$w_{pg} = w_{\text{by the gas}} = \int_{V_i}^{V_f} P dV$$

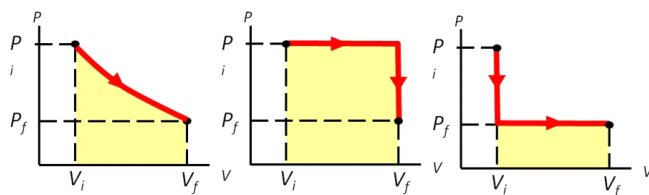
The only difference is the minus sign. We are going to have to be careful!

Still, this looks easy enough, but to integrate we must know how  $P$  depends on  $V$  during the whole process. It was simple for an isobaric process, but it could be much harder for other processes. We can plot  $P$  vs.  $V$  to see how it varies for a process. We would expect the integral to be the area under a  $PV$  curve. This is very like mechanical work, which was the area under the  $F$ - $x$  curve.



We can make a general statement: The work done on a gas in a quasi-static process that takes the gas from an initial state to a final state is the negative of the area under the curve on a  $PV$  diagram evaluated between the initial and final states.

Unfortunately, the work done depends on the shape of the curve on the  $PV$  diagram. Several are shown below. Each has a different amount of work done (notice the different areas under the curves), but the same initial and final points.



Notice that we have calculated the amount of work done on the gas. For physicists this is normally what we want.

You might be wondering if that is what we want to build car or jet engines. Don't we want the gas to expand to push the piston and make the car go? And of course, you are right in your thinking. Eventually we want to know the work done by the gas on the piston,  $w_{pg}$ . But for now, we will look at  $w_{gp}$ . But from what we have done we know these two works are very related for a quasi-static process.

$$w_{\text{on the gas}} = -w_{\text{by the gas}}$$

But let's go back to our first law of thermodynamics.

$$\Delta E_{int} = Q + w_{int} \quad (34.11)$$

We know how  $w_{int}$  changes on a PV diagram. How do  $\Delta E_{in}$  and  $Q$  change on a PV diagram? For energy transfer by heat, we don't need a pressure or volume change, so a PV diagram isn't a great way to show  $Q$ . But we can consider  $\Delta E_{int}$  on a PV diagram. We already know that for ideal gasses

$$E_{int} = \frac{3}{2}k_B T \quad (34.12)$$

So  $E_{int}$  changes with  $T$ . But there is no  $T$  on a PV diagram! For ideal gasses we can solve this problem. Suppose we have  $n$  moles gas in a cylinder. We can solve for  $P$  as a function of  $V$

$$P = \frac{nRT}{V}$$

Now we want to let  $T$  be constant. Along a line of constant  $T$  our  $E_{int}$  will be constant.

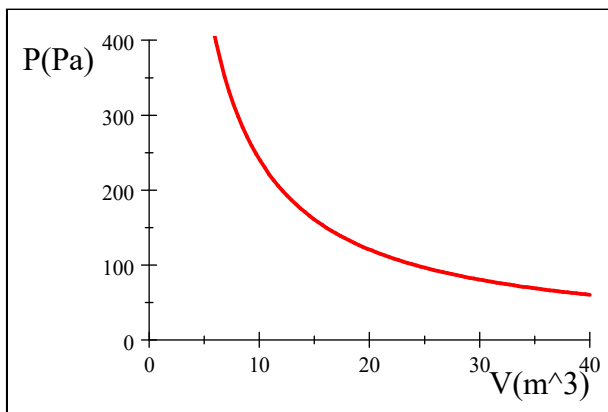
$$P = (nRT) \frac{1}{V}$$

everything in the parenthesis is constant so

$$P \propto \frac{1}{V}$$

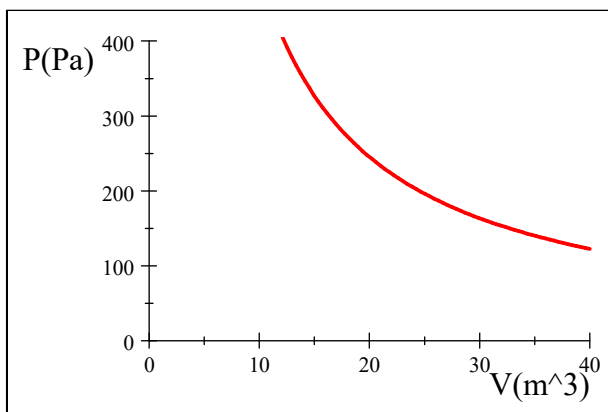
We can plot this for

$n = 1 \text{ mol}$	number of moles
$R = 8.314 \frac{\text{J}}{\text{mol K}}$	Universal gas constant
$T = 290 \text{ K}$	Temperature in Kelvins

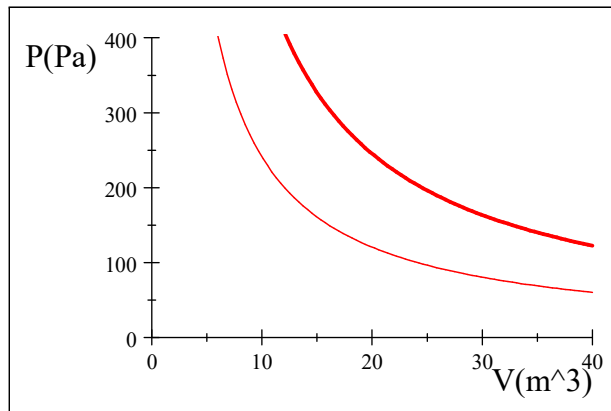


All along this line  $T$  is constant so  $E_{int}$  is constant. We have already seen such a line on a PV diagram and know it is called an *isotherm*. Now let's plot it again for a different value of  $T$

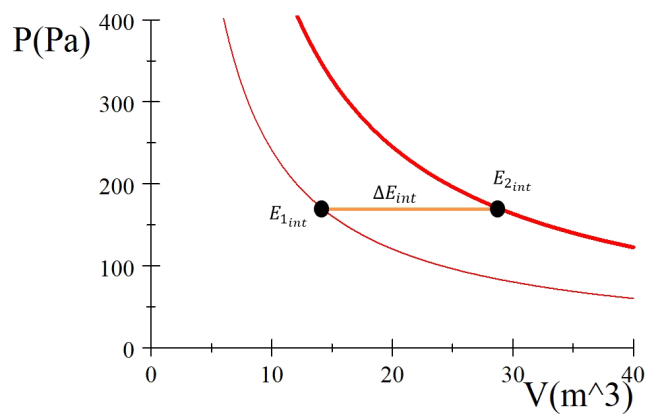
$n = 1 \text{ mol}$	number of moles
$R = 8.314 \frac{\text{J}}{\text{mol K}}$	Universal gas constant
$T = 590 \text{ K}$	Temperature in Kelvins



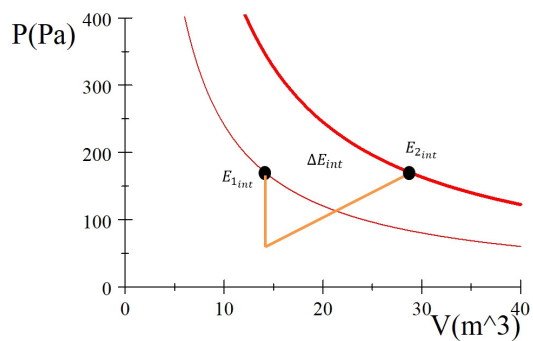
Notice that the curve looks like the same shape, but it has been shifted toward the upper right hand corner of the graph. If we place both the  $T = 290$  and  $T = 590$  graphs on the same plot, we can better see the shift.



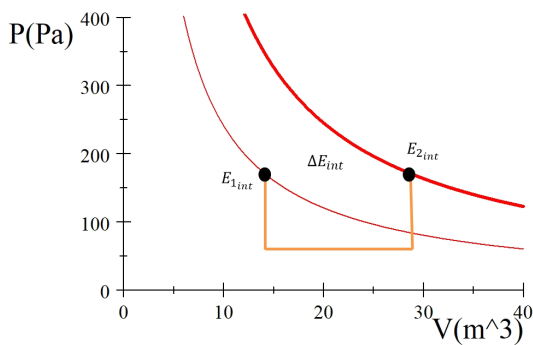
The dark curve is our new pot. The light curve is the old plot for comparison. The curves look a lot alike. They are essentially the same shape. But their location (how far they are from the origin) depends on the temperature, with warmer temperatures moving to the upper right hand part off the graph. So our  $P$  vs.  $V$  graph can tell us something about temperature. And because  $E_{int} = \frac{3}{2}k_B T$  these lines and their positions also tell us about the internal energy. A change in internal energy would be going from one such isothermal line to another.



And because  $\Delta E_{int}$  is path independent, it doesn't matter how we go from  $E_{int}$ . So if we followed this PV path



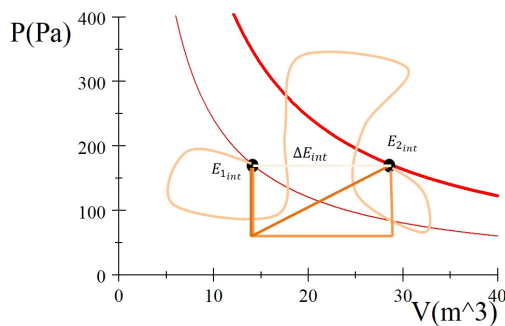
or this PV path



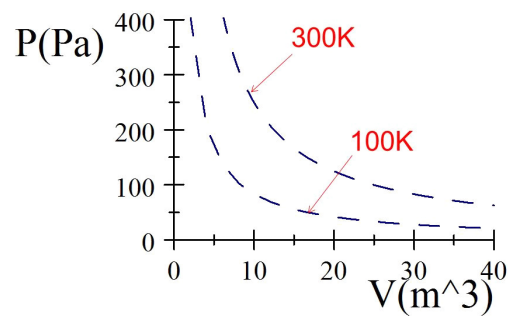
we would get the same  $\Delta E_{int}$ . A way to think about this is that  $\Delta E_{int}$  only depends on its starting and end points (think about displacement). So

$$\Delta E_{int} = E_{2_{int}} - E_{1_{int}}$$

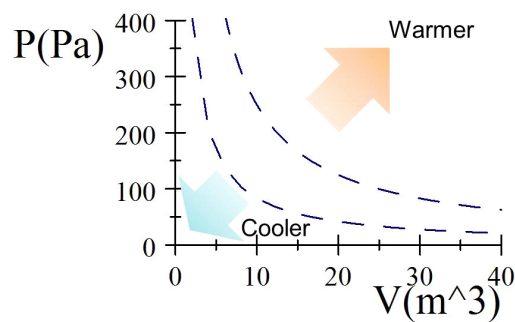
regardless of the path. So any path from  $E_{1_{int}}$  to  $E_{2_{int}}$  gives the same change in internal energy.



Looking at an isothermal process can help us understand our other processes. Suppose we have two different isothermal processes, one at 100 K and one at 300 K. The isotherms look like this on a  $PV$  diagram:



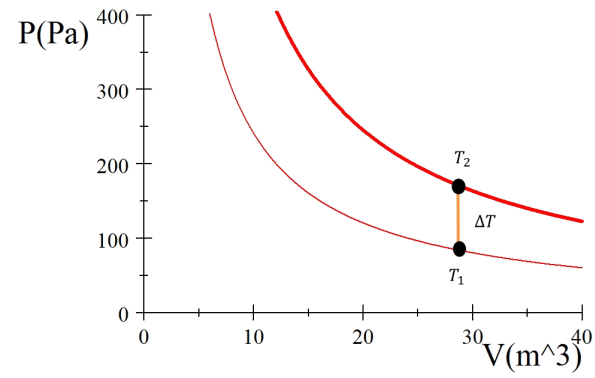
Every point on the 300 K line has the same temperature. Every point on the 100 K line has the same temperature. We can see that points on the  $PV$  diagram that are closer to the origin must have lower temperatures. We can see the points farther from the origin have higher temperatures.



Let's go back to energy transfer by heat. We know

$$Q = nC_v\Delta T$$

if the volume doesn't change, we now can see a way to determine  $Q$  from a  $PV$  diagram.



But this is just for a process where volume doesn't change. Still, our PV diagram does seem to be useful for thinking about thermodynamic process and for filling in our first law equation

$$\Delta E_{int} = Q + w$$

We will work with this some more in our next lecture.