

Chapter 35

35 Thermodynamic Processes 2.3.4, 2.3.5

We found in our last lecture that the first law of thermodynamics gives us the change in internal energy

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

and that we could illustrate the work, w , process on a PV diagram and we even found a way to show ΔE_{int} on a PV diagram. We did find a way to show Q for the special case of a process that doesn't change volume. But that seems so specific. Aren't there infinite different paths from a specific initial internal energy, $E_{i_{int}}$ to a final internal energy, $E_{f_{int}}$? Of course, the answer is yes. But many of these paths from $E_{i_{int}}$ to $E_{f_{int}}$ would require a numerical solution (this means use a computer to do the calculation). So instead, we are going to learn a few special processes that are easy to calculate by hand. We will limit our study mostly to these special processes. In industry you might need to go beyond these simple processes, but they give us great insight into how internal energy changes and we can even use them (mostly) to understand complicated systems like gasoline engines. So let's get started and define our special processes.

Fundamental Concepts

- There is a sign convention for energy transfer. If energy leaves it is negative, if it comes into the system it is positive.
- There are two molar specific heats for gasses, C_V and C_P .
- The two molar specific heats are related $C_P = C_V + R$
- There are four special processes for which it is easy to find ΔE_{int} , Q , and w , and three of them are isochoric, isobaric, and isothermal
- For an isochoric process $w_{int} = 0$, $Q = nC_V\Delta T$, $\Delta E_{int} = nC_V\Delta T$

- For an isobaric process $w_{int} = -P\Delta V$, $Q = nC_P\Delta T$, $\Delta E_{int} = nC_P\Delta T - P\Delta V$
- For an isothermal process $w = -nRT \left[\ln \frac{V_f}{V_i} \right]$, $Q = -w$, $\Delta E_{int} = 0$

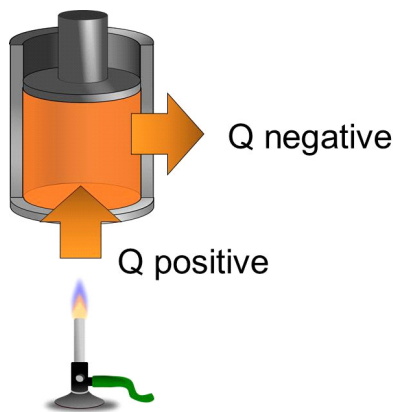
35.1 Heat and systems

Heat is a transfer of energy, so it can't be a property of the system, itself. It is an interaction of the system with its environment. This means that heat is not a state variable. It will depend on process path on a PV-diagram, like work does. Only the combination

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

is path dependent.

It is customary to refer to energy gained from an environment as positive heat, and energy lost to the environment as negative heat.



This is a sign convention. We could totally define this the other way. But it is useful for everyone to agree to one system of signs, and the system used in physics today is that energy is negative when it leaves a system, and positive when it enters a system. We will need to remember this for our problems.

It is useful to compare the sign convention for heat with that we built for work (on the gas).

	Work	Heat
Interaction mechanism	Mechanical	Thermal
Process	Macroscopic forces acting on the system	Microscopic collisions between gas particles in the system
Process Requires	External force and displacement	Temperature Difference
Positive when	A gas is compressed: mechanical energy is transferred in to system	The environment is at a higher temperature than the system
Negative when	A gas expands: mechanical energy is transferred out of the system	The environment is at a lower temperature than the system
Equilibrium condition	No net force or torque on the system	System and environment are at the same temperature

Just like with work, the definition of the word “heat” takes some practice to get used to.

Question 123.11.2

It is really important to not use the word “heat” as we use the word “temperature.” Temperature is proportional to the internal energy,

Question 123.11.3

Question 123.11.4

$$E_{int} \propto T$$

as we will show soon. But Q is a transfer of energy. A gas can “have” a temperature, but it “experiences” a transfer of energy. That is why it shows up in the first law as a mechanism for the change in internal energy.

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

This is not intuitive because of our left-over language from the caloric theory. So we must continually be on our guard, because poor language leads to poor decisions in experiments and engineering designs.

It would help if we all said things like “to do heat” instead of “heat” when we are warming things. That is what we do with work. We “do work” so we should “do heat,” and this may be a good way to think about it, even though to say “do heat” like this would make our roommates wonder.

Question 123.11.5

We now know that ΔE_{int} is a state variable. It does not depend on path. But it is just one of many state variable for a gas. For ideal gasses, we have

$$P, V, n, T, \Delta E_{int}$$

all as state variables. It takes all of these quantities to describe an ideal gas.

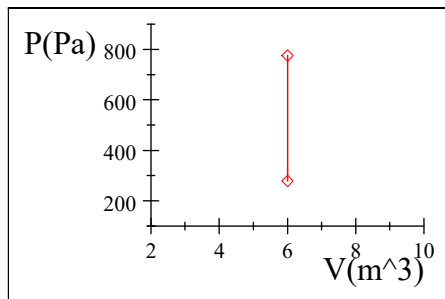
For example, we know that

$$E_{int} \propto T$$

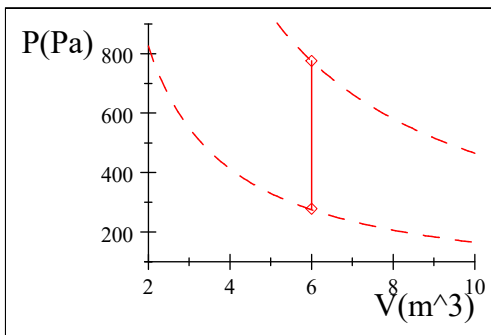
but this does not tell us ΔE_{int} . The quantity ΔE_{int} only tells us about the change in E_{int} . We cannot tell what path was used to accomplish ΔE_{int} . So our first law does not tell us P , V , or n either. We will have to use the first law in cooperation with the ideal gas law.

35.1.1 Constant Volume Process

We ended our last lecture with a constant volume process. But we didn't give it a name. A constant volume process is called an *isochoric process*. Suppose we have a process that takes us between two states on a PV diagram as shown in the next figure.



We start at one pressure, say $P = 275$ Pa, and end at another pressure, say, $P = 775$ Pa. In this process, notice that the volume does not change. Would we predict that the temperature went up or down in taking this path? Well, we went from the lower to the upper part of the graph, so we expect that the temperature went up. We could check this by plotting the two isotherms that cross through our points.



Sure enough, our temperature went up. Starting again with the ideal gas law

$$P = \left(\frac{nR}{V} \right) T$$

we can see that when V is constant, P goes like T , so if P went up, so did the temperature.

For this isochoric type process no work is done.

$$w_{\text{on the gas}} = w_{\text{int}} = - \int_{V_i}^{V_f} P dV$$

but V doesn't change so $dV = 0$. and therefore

$$w_{\text{int}} = 0$$

But we do have energy transfer by heat

$$Q = nC_v\Delta T$$

so for our first law

$$\begin{aligned}\Delta E_{int} &= Q + w \\ &= nC_v\Delta T + 0 \\ &= nC_v\Delta T\end{aligned}$$

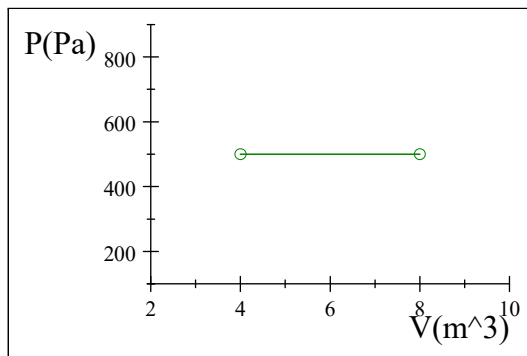
That seems useful! But how would create such a situation? Consider what would happen¹ if you placed an aerosol can in a fire. The aerosol can is rigid, so the volume can't change. But the fire will make the temperature change, and the pressure will change—that is—until the can explodes.

We will also need our differential form for the first law for isochoric processes.

$$dE_{int} = nC_v dT$$

35.1.2 Constant Pressure Process

But there is more than one way to add energy to a gas. Suppose we envision another process where instead of keeping the volume constant we keep the pressure constant.



We have already considered this process. We called it an *isobaric process*. We found that the work done in an isobaric process is

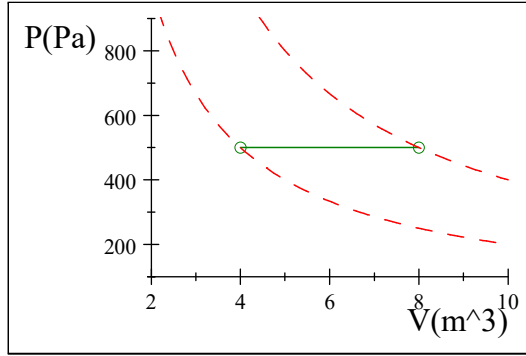
$$w_{\text{on the gas}} = -P(V_f - V_i)$$

¹Only consider this, because it would be irresponsible and dangerous (and illegal in some states) to do this!

Let's review that here

$$\begin{aligned}
 w_{int} &= - \int_{V_i}^{V_f} P dV \\
 &= -P \int_{V_i}^{V_f} dV \\
 &= -P (V_f - V_i) \\
 &= -P \Delta V
 \end{aligned}$$

We can see that in this process the pressure is not changing. If we go from left to right along this path, will the temperature rise? We know that going to the right means higher temperature on a PV diagram, so yes it will.



For isochoric processes we defined a molar heat capacity at constant volume C_V that let us find Q

$$Q = nC_V \Delta T$$

In our differential first law equation

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

and we found that for isochoric processes no work was done so

$$dE_{int} = dQ = nC_v dT$$

but for an isobaric process we have

$$dE_{int} = dQ - PdV$$

But what do we do for dQ if the process is isobaric? It turns out we can play the same trick. Let's define a *molar heat capacity at constant pressure*, C_P . Then

$$Q = nC_P \Delta T$$

and

$$dQ = nC_P dT$$

We found that for idea gasses

$$C_V = \frac{3}{2}R$$

we need to find a value for C_P . Let's use our ideal gas law

$$PV = nRT$$

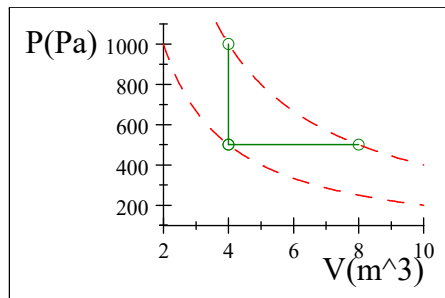
and let the volume and Temperature change, but not P nor n .

$$P\Delta V = nR\Delta T$$

and for an isobaric process, this is our work! Our differential first law would be

$$\begin{aligned}\Delta E_{int} &= Q - w \\ &= nC_P\Delta T - nR\Delta T \\ &= n(C_P - R)\Delta T\end{aligned}$$

But dE_{int} is the same for any two processes that go between the same two temperatures. Suppose we look at a situation where we have the same ΔE_{int} but we make the change two ways, one with an isochoric process and one with an isobaric process.



We already know that for the isochoric process

$$\Delta E_{V_{int}} = nC_v\Delta T$$

Then since

$$\begin{aligned}\Delta E_{V_{int}} &= \Delta E_{P_{int}} \\ nC_v\Delta T &= n(C_P - R)\Delta T\end{aligned}$$

and we can cancel the n 's and the dT 's.

$$C_v = (C_P - R)$$

which gives

$$C_P = C_V + R$$

for an ideal gas. So if we know either C_P or C_V for a gas, we can always find the other. This works pretty well in practice for monotonic gasses (and even for diatomic gasses) at standard temperature and pressure. Not only can we find Q_V and Q_P with molar specific heats, but if we know one molar specific heat, we can easily calculate the other! Since

$$C_V = \frac{3}{2}R$$

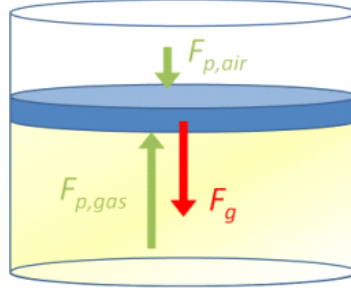
then we know

$$C_P = \frac{5}{2}R$$

So for an isobaric process we have

$$\begin{aligned}\Delta E_{int} &= Q + w \\ &= nC_P\Delta T - P\Delta V\end{aligned}$$

How would we produce such a situation? We saw this in our last lecture, but let's think about it again. Consider a piston in a cylinder. The cylinder has a gas inside, and air on the outside



The piston is free to move up or down. The forces acting on the piston are shown. The weight of the piston pulls it downward, the force due to pressure of the gas, $F_{p,gas}$ pushes up, and the air pressure $F_{p,air}$ pushes down. The net force will be

$$\Sigma F_y = ma_y = F_{p,gas} - F_{p,air} - mg$$

where the mass of the piston is m . We can write this as

$$ma_y = P_{gas}A - P_{air}A - mg$$

If the piston is not accelerating, then

$$P_{gas} = P_{air} + \frac{mg}{A}$$

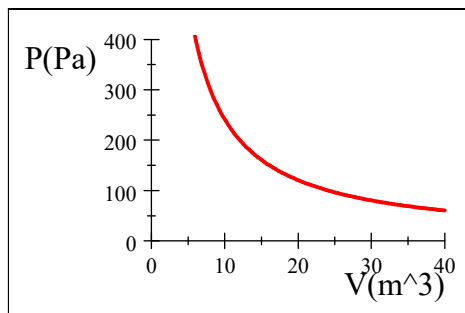
and we find that the pressure of the gas inside is slightly larger than the outside air pressure. What would happen if we heated the gas?

$$PV = NRT$$

would suggest that P might change, but since the piston is free to move, what happens is that the force $F_{p,gas}$ increases when P_{gas} increases, and the piston accelerates upward. It stops when the forces are again balanced. But that means that P_{gas} will only change for a moment, and then we will achieve equilibrium at the same old value of P_{gas} . But something has changed, the volume has increased.

35.2 Constant Temperature Process

We have already done quite a bit of work on this process in our last lecture



We found that $\Delta E_{int} = 0$ for an isothermal process. Then

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

gives

$$Q = w$$

but we need to find w . Let's use our ideal gas law for this again.

In this case we know T and n , and that we know P_i and V_i and P_f and V_f . Can we find ΔE_{int} , Q , and w ?

We already know how to find w

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

so from our work equation

$$w_{int} = - \int_{V_i}^{V_f} P dV \quad (35.1)$$

$$= - \int_{V_i}^{V_f} \frac{nRT}{V} dV \quad (35.2)$$

$$= -nRT \int_{V_i}^{V_f} \frac{1}{V} dV \quad (35.3)$$

$$= -nRT \ln V \Big|_{V_i}^{V_f} \quad (35.4)$$

$$= -nRT [\ln (V_f) - \ln (V_i)] \quad (35.5)$$

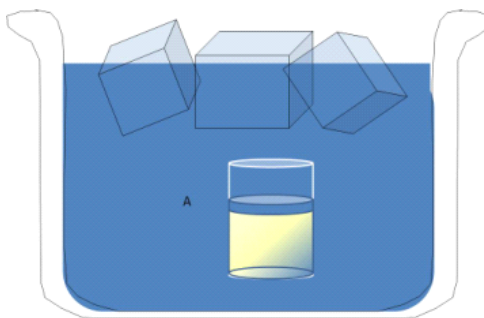
$$w = -nRT \left[\ln \frac{V_f}{V_i} \right]$$

So then

$$\begin{aligned} Q &= -w \\ &= nRT \left[\ln \frac{V_f}{V_i} \right] \end{aligned}$$

and we did not need our molar specific heat equations for this process.

How do we make such a path happen? Consider our piston again.



This time, let's put it in a vat of ice water. We can compress the gas by pushing on the piston. But if the temperature is changed by compressing the gas, it is quickly changed back by the ice water.

We have ΔE_{int} , Q , and w for three of our special processes. This completes three of our four special processes!