

(1) An ideal gas has the equation of state  $PV = NkT$  where  $N$  is the number of molecules,  $k$  is Boltzmann's constant ( $k=1.380 \times 10^{-23}$  J/K). This may also be written as  $PV = nRT$  where  $n$  is the number of moles and  $R=8.314$  J/(K mol).  $T$  in either expression must be in Kelvin. An ideal gas goes through an **isobaric** ( $P=\text{constant}$ ) change in volume. If  $P=1$  atm, and the change in volume is  $-1$  m<sup>3</sup>, what is the work done by the gas?

(2) An ideal gas goes through an **isothermal** ( $T=\text{constant}$ ) process in which the change in volume was  $+2$  m<sup>3</sup>. (a) What is the change in internal energy of the ideal gas? (b) What is the work done by the gas?

(3) An ideal gas undergoes an **isovolumeric** process ( $V=\text{constant}$ ) with the addition of  $Q$  amount of heat. What is the change in internal energy of the system? Did the temperature of the system change?

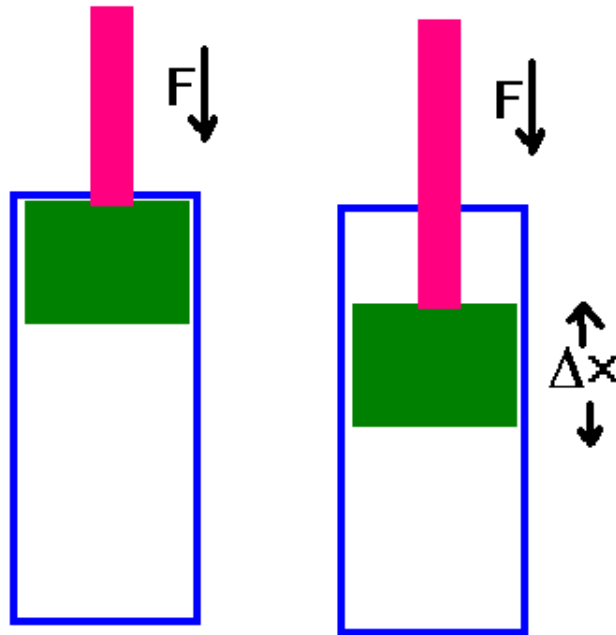
(4) 1 kg of ice is initially at  $-30$  C. How much heat must be supplied in order to make steam at  $130$  C? You may assume the atmospheric pressure here is 1 atmosphere. Then, what is the change in internal energy for the water?

(5) How much ice at  $0$  C would you have to put into 1 kg of boiling water to make a mixture which has an equilibrium temperature of  $75$  C?

**Thermodynamic work, The 1st law of thermodynamics and 1st order changes of state**

Note: I have chosen my words in this section very carefully. It is very important to distinguish between the system and the environment in your understanding.

Thermodynamic work is defined in the same way as we defined it for mechanics: Consider a **constant force** acting through a distance  $x$  on a plunger:



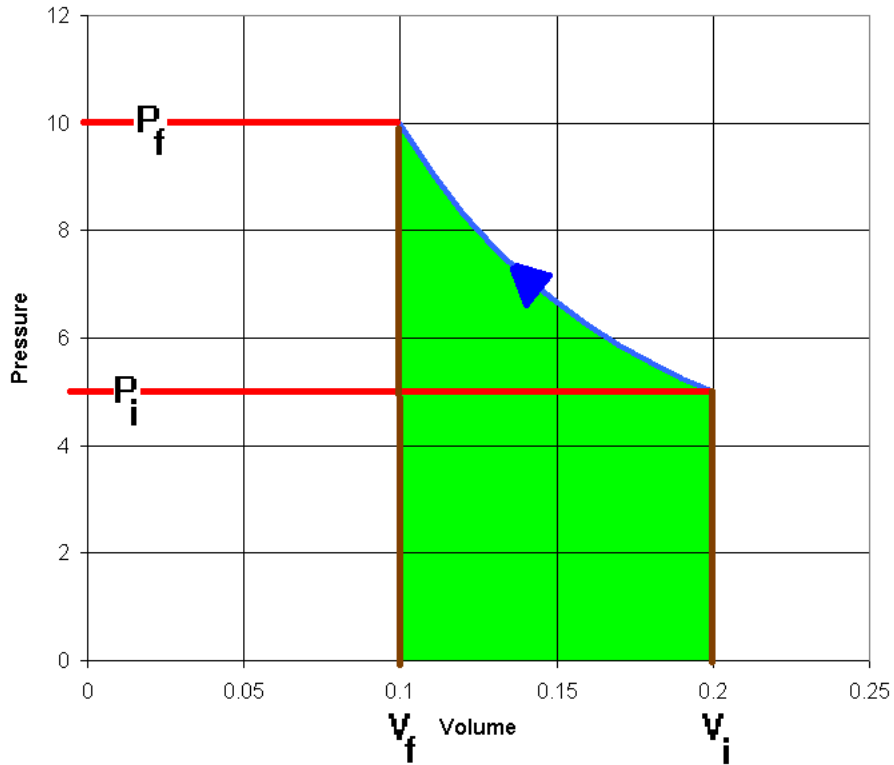
The work **done on the system** is given by  $W = F(\Delta x)$ . Suppose the plunger has an area  $A$ . Let's multiply and divide by this area:  $W_{\text{on system}} = \frac{F}{A}(\Delta x)A = P(\Delta V)$ .

**Emphasis:**

$W$  in our discussions represents the work **done by a system** on its surroundings.

Now, we have to choose: a system can do work or the system can have work done on it. One of these has got to be positive and one is negative. **Physicists choose the work to be negative if the system has work done upon it.** Since the work term is zero unless the volume changes, this implies thus a compression. The work is positive if the system does the work. This implies an expansion. Other conventions will need to be worked out if your system does not involve  $P, T$  and  $V$  only (this is the case for magnetic or electrical systems).

We imagine that in general we can have both the pressure and the volume change. The question is how to calculate the work done on the gas in this situation? Let's see:



The answer is to find the area under the P-V curve in any way you can. In this **particular** diagram above, the work done by the gas is then negative of the absolute value of this area. Since the volume decreased, the system had work done on it. By our convention, then the work done by the system is thus negative. Ok, that part is clear I think. Now to calculate the work done by the system here, we need to add up the small amounts of work done over the path that the process went through. Thus:

$$W = \sum_i P_i (\Delta V_i)$$

For non-calculus students, it is easy to calculate this so long as only one of the thermodynamic variables changes. When both thermodynamic variables change, I will need to give you the results that are obtained from calculus.

In general you can not say how much work was done by the system if P and V are both changing. In fact, in order to evaluate the amount of work done, it is essential that you know the path that the process took since that path that will give you the relationship between P and V.

Now, let's think back to a problem from an earlier worksheet ...

(4) Aluminum has a coefficient of linear expansion of  $24 \times 10^{-6} / ^\circ\text{C}$  and the specific heat of aluminum is  $900 \text{ J}/(\text{kg } ^\circ\text{C})$ . Suppose a block of aluminum of  $10 \text{ cm}$  on a side has a density of  $2.7 \times 10^3 \text{ kg}/\text{m}^3$ . We are going to expand this aluminum in a vacuum for reasons that will become clear in later lectures. The aluminum is heated from a temperature of  $0^\circ\text{C}$  to a temperature of  $100^\circ\text{C}$ . How much heat is added to the system? How much is the final volume of the block?

Thermodynamic work is defined by  $W = P\Delta V$ . If the bar were expanded against atmospheric pressure, how much work did the bar do in the expansion?

Solution:

The amount of heat added is given by:

$$Q = m_{\text{al}} c_{\text{al}} (\Delta T)$$

We're not given the mass directly here but it is given by:

$$m_{\text{al}} = \rho_{\text{al}} V_{\text{al}} = (2.7 \times 10^3 \frac{\text{kg}}{\text{m}^3})(0.1\text{m})^3 = 2.7\text{kg}$$

The amount of heat added to the system is then given by:

$$Q = (2.7\text{kg})(900 \frac{\text{J}}{\text{kg}^\circ\text{C}})(100^\circ\text{C}) = 2.43 \times 10^5 \text{ J}$$

The change in volume is given by:

$$\Delta V = V_0 (3\alpha)(\Delta T) = (0.1)^3 (3 \times 24 \times 10^{-6})(100) = 7.2 \times 10^{-6} \text{ m}^3$$

The final volume is then  $V = V_0 + \Delta V = 1.0072 \times 10^{-3} \text{ m}^3$

The thermodynamic work done in expanding against the atmosphere is:

$$W = P(\Delta V) = 1.013 \times 10^5 \text{ Pa}(7.2 \times 10^{-6} \text{ m}^3) = 0.73 \text{ J}$$

Now in this case let's consider that the block is heated against the atmospheric pressure. Clearly the amount of work that the block did in no way even come close to the amount of heat added to the system. One must, therefore, ask just where did this energy go?

This particular question brings us up to the point where we need to specify where it went ... it went into what is called the internal energy of the system. We clearly have the statement of what is then the first law of thermodynamics: ( $U$  is internal energy)

$$\Delta U_{\text{system}} = U_{\text{final}} - U_{\text{initial}} = Q - W_{\text{done by system}}$$

This makes a lot of sense when you see how I've defined this ... it is a statement of energy conservation and, in words is this:

whatever heat was added to a system that did not result in work done by the system went into changing the internal energy of the system in such a way that energy was conserved.

(aren't you now glad we can use math in this course?)

Now, we're ready to make our first calculation:

For the block above, what was the change in internal energy?

Here, the work done by the system was  $+0.73 \text{ J}$ .

The amount of heat added to the system was  $2.43 \times 10^5 \text{ J}$

Therefore the change in internal energy of the system was:

$$\Delta U = 2.43 \times 10^5 \text{ J} - 0.73 \text{ J} = 2.43 \times 10^5 \text{ J}$$

In fact, almost all the heat went into changing the internal energy of the system.

## Changes of phase

At the offset, I'll say that there are many types of thermodynamic systems: magnetic, electrical, gas, solids, plasmas, etc. While we'll basically concentrate on gases, don't forget that this same theory has more wide appeal than what we talk about.

There are also many types of phase transitions. The particular phase transitions that we consider in this course, we term as "first order" phase transitions. These phase transitions are accompanied by a **Latent Heat, L** which is that amount of heat which needs to be added to or removed from a substance to make it go through a phase transition. For our first order phase transitions, the temperature at which the transition occurs will be a constant and the system is assumed to stay at this temperature until the entire phase transition has been completed.

Let's see how to do calculations involving latent heat.

(a) Melt ice: A block of ice of mass  $m$  at 0 C becomes water at 0 C. How much heat was added to the system? Answer:  $Q = mL_f$  (latent heat of fusion).

(b) Boil water: A mass  $m$  of water at 100 C becomes steam at 100 C. How much heat was added to the system? Answer  $Q = mL_v$  (latent heat of vaporization)

There is one additional very important point that I'd better introduce before we get too far along. This is the Kelvin temperature scale.

$$\text{Kelvin: } T_{\text{kelvin}} = 273.15 + T_{\text{centigrade}}$$

The Kelvin temperature scale is the scale that you really want to be using when you are calculating thermodynamic state functions (such as entropy). **Do not use centigrade scales for any thermodynamic state function calculation (such as U, S, etc.) directly involving units of temperature!**

One final note about our gasses: they don't leak and the number of molecules of our gasses will remain constant. Our gasses also don't undergo chemical reactions that would change the number of molecules. Be careful when this is not true because you need to introduce a new thermodynamic potential function. You'll hear more about this in the second semester of Physical Chemistry.

(1) An ideal gas has the equation of state  $PV = NkT$  where  $N$  is the number of molecules,  $k$  is Boltzmann's constant ( $k=1.380 \times 10^{-23}$  J/K). This may also be written as  $PV = nRT$  where  $n$  is the number of moles and  $R=8.314$  J/(K mol).  $T$  in either expression must be in Kelvin. An ideal gas goes through an **isobaric** ( $P=\text{constant}$ ) change in volume. If  $P=1$  atm, and the change in volume is  $-1 \text{ m}^3$ , what is the work done by the gas?

Solution: Since the pressure is constant, the work is easy to calculate here. The work done by the gas is given above:

$$W_{\text{done by system}} = P(\Delta V)$$

But here the volume decreases and  $\Delta V = -1 \text{ m}^3$ . This means that the work done will be ultimately negative. Since this is done against a constant pressure of 1 atmosphere ( $1 \times 10^5$  Pa), we thus have the work done by the system is  $W = -1 \times 10^5$  J.

We can not presently say what the change in internal energy of the gas is. This will come. For now, you need to practice saying "**for an ideal gas, the internal energy is a function of temperature only.**"

**N Symbol review:**

$N$ =Number of molecules (or atoms for mono-atomic systems)

$n$ =Number of moles

$N_A$ =Avogadro's Number

The  $N$ s are related by:

$$N = nN_A$$

(2) An ideal gas goes through an **isothermal** ( $T=\text{constant}$ ) process in which the change in volume was  $+2 \text{ m}^3$ .

(a) What is the change in internal energy of the ideal gas?

Since "**for an ideal gas, the internal energy is a function of temperature only,**" we have no choice but to say that  $\Delta U = 0$ .

(b) What is the work done by the gas?

Non-calculus students: Here is a useful thing for you to remember. It will come back for us to use time and time again: Suppose you have a function which appears as:

$$\frac{\Delta V}{V}, \text{ or more precisely } \sum_i \frac{\Delta V_i}{V_i}$$

and you want to use this over a large range of the variable  $V$  (from, say  $V_i$  to  $V_f$ ). This function can be approximated as

$$\frac{\Delta V}{V} \approx \ln\left(\frac{V_f}{V_i}\right), \text{ or more precisely, } \sum_i \frac{\Delta V_i}{V_i} \approx \ln\left(\frac{V_f}{V_i}\right)$$

This is a horrendous abuse of mathematics. Probably that's why I like to use it so much. Keep this very useful mathematical approximation in mind. Now I'll show you how to use

it. The work done by the gas in this problem is given by  $W=P\Delta V$ . The problem here is  $P$  is changing.

Solving the **ideal gas equation of state** for  $P$ , we find:

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

So the work done is

$$W = NkT \left( \frac{\Delta V}{V} \right), \text{ or more precisely, } W = NkT \sum_i \left( \frac{\Delta V_i}{V_i} \right)$$

Here, you are going from an initial volume to a final volume. This allows a re-expression of this result (using the useful approximation I've given you) as:

$$W = NkT \ln \left( \frac{V_f}{V_i} \right)$$

Ok, we've now found the work required for the gas to undergo an isothermal expansion. How much heat was supplied for this to happen? (and yes, you might say Wow! put in heat, the temperature stayed the same and no phase transition occurred).

Well since  $\Delta U=0$ , we have no choice but to conclude from the first law that  $Q=W$ . Probably it is somewhat important to point out here that if heat is added, an expansion must have resulted. If heat was removed, a compression must have resulted. Again, this work **refers to an Ideal Gas** ... not a block of rubber (add heat to rubber and it might get smaller)! By saying (above) the equation of state for the ideal gas, we have really narrowed our range of systems at this point.

(3) An ideal gas undergoes an **isovolumeric** process ( $V=\text{constant}$ ) with the addition of  $Q$  amount of heat. What is the change in internal energy of the system? Did the temperature of the system change?

Solution: From the first law of thermodynamics,

$$\Delta U_{\text{system}} = U_{\text{final}} - U_{\text{initial}} = Q - W_{\text{done by system}} .$$

Further, since there is no volume change, we must conclude that no work was done (**IDG only!**). Hence we are left with  $\Delta U=Q$ . Since this is an ideal gas and since **for an ideal gas, the internal energy is a function of temperature only,** the temperature must have changed. We are not yet in a position to say by how much until we look at the kinetic theory of an ideal gas.

(4) 1 kg of ice is initially at -30 C. How much heat must be supplied in order to make steam at 130 C? You may assume the atmospheric pressure here is 1 atmosphere. Then, what is the change in internal energy for the water?

Solution:

(a) You must heat the ice up to 0 C. The specific heat of ice is about 2090 J/(kg C). Thus:

$$Q_1 = mc\Delta T = 1(2090)(30) = 6.27 \times 10^4 \text{ J}$$

(b) You must convert the ice into water at 0 C. The latent heat of fusion of water is  $3.33 \times 10^5$  J/kg.

$$Q_2 = mL_f = 1(3.33 \times 10^5) = 3.33 \times 10^5 \text{ J}$$

(c) You must heat water from 0 C to 100 C. The specific heat of water is 4186 J/(kg C).

$$Q_3 = mc\Delta T = 1(4186)(100) = 4.186 \times 10^5 \text{ J}$$

(d) You must convert water into steam at 100 C. The latent heat of vaporization of water is  $2.26 \times 10^6$  J/kg.

$$Q_4 = mL_v = 1(2.26 \times 10^6) = 2.26 \times 10^6 \text{ J}$$

(e) You must raise the temperature of the steam. The specific heat of steam is  $2.01 \times 10^3$  J/(kg C).

$$Q_5 = mc\Delta T = 1(2.01 \times 10^3)(30) = 6.03 \times 10^4 \text{ J}$$

And ... you've got to worry about losing some of your heat overall to work in pushing away the atmosphere (which means you'll have to add some extra heat to the system so it can do this work). Let's find out how much this requires, and how important it is.

$W = P\Delta V$ . The change in volume here is  $\Delta V = V_{\text{gas}} - V_{\text{liquid}}$  approximately. I'm assuming that the ice and the water are about the same volume. What is the volume of the steam? We'll assume the ideal gas equation of state here, but we've got to find N. How?

1 kg of water has how many molecules is the question that we've got to answer.

We know that the chemical formula for water is  $\text{H}_2\text{O}$  and the molecular weight of a water molecule is about  $16 + 2 = 18$  g/mole. 1 mole has  $6.02 \times 10^{23}$  particles.

$$n = m_{\text{water}} \left( \frac{1 \text{ mole}}{18 \text{ g}} \right) \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) = 55.6 \text{ moles}$$

$$N = nN_A = (55.6 \text{ moles}) \left( \frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mole}} \right) = 3.34 \times 10^{25} \text{ molecules}$$

The volume of the gas is then given by:

$$V = \frac{NkT}{P} = \frac{(3.34 \times 10^{25})(1.380 \times 10^{-23})(403.15)}{1 \times 10^5} = 1.86 \text{ m}^3$$

The volume of the liquid was  $V = \frac{m}{\rho} = \frac{1}{1000} = 1 \times 10^{-3} \text{ m}^3$

The work done is then:  $W = P(V_{\text{gas}} - V_{\text{liquid}}) = 1 \times 10^5 (1.86 - .001) = 1.86 \times 10^5 \text{ J}$

Now, you've really got to be careful at this point and understand the physics: The latent heats that I've given you **are specified at 1 atmosphere**. This means that any additional heat that needs to be supplied to push the atmosphere away has already been accounted for in that value of the latent heat.

How much total heat had to be added?

$$Q = \sum_{i=1}^5 Q_i = 6.27 \times 10^4 + 3.33 \times 10^5 + 4.186 \times 10^5 + 2.26 \times 10^6 + 6.03 \times 10^4$$

So,

$$Q = 3.13 \times 10^6 \text{ J}$$

In this problem, about 6% of the heat input went into doing work to push the atmosphere out of the way.

How do I know that I'm right about the extra energy being required to get the same results? Imagine a really big pressure that you're trying to vaporize the steam against. It simply won't do it unless you add more heat. This is exactly the opposite of the case where you try to cook something in boiling water on top of a high mountain. Almost everyone knows that water boils at a lower temperature on mountain tops. Indeed, you may be lucky enough to see sometime what happens to water when a complete vacuum is pulled on it suddenly.

Now let's try to answer the really hard question: What is the change in internal energy of the water?

The first law of thermo says:

$$\Delta U_{\text{system}} = U_{\text{final}} - U_{\text{initial}} = Q - W_{\text{done by system}}$$

$$\Delta U = 3.13 \times 10^6 \text{ J} - 1.86 \times 10^5 \text{ J} = 2.944 \times 10^6 \text{ J}$$

(ok, it wasn't all that hard after all).

Again: the first law of thermodynamics is true independent of the system of application.

(5) How much ice at 0 C would you have to put into 1 kg of boiling water to make a mixture which has an equilibrium temperature of 75 C?

Solution:

Energy is conserved. Thus:  $Q = 0$ .

So, we have:

$$\begin{aligned} m_i L_f + m_i c (T - T_m) + mc (T - T_w) &= 0 \\ m_i (3.33 \times 10^5) + m_i (4186)(75) + 4186(-25) &= 0 \\ m_i (3.33 \times 10^5) + m_i 313950 - 104650 &= 0 \\ m_i &= 0.16 \text{ kg} \end{aligned}$$

It is important to realize here that the Q which I am using here is the net heat added to a total system surrounded by a perfectly insulating wall: It is necessarily zero. The total system in this case is the boiling water and the ice cube. Another interesting observation: boiling, like evaporation, is a cooling process: both are removing large amounts of heat from the system. In boiling, however, the heat that is being removed comes from a heater (like a stove) supplying heat to the water. In evaporation, it is the faster molecules that are leaving the water. In this problem, however, the boiling was used only to fix the temperature of the water at 100 C.