

The First Law of Thermodynamics

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1 Introduction

Classical thermodynamics is mainly concerned with the transformation of work into heat and of heat into work. Today's topic, the first law of thermodynamics, describes the equivalence of the two and the conservation of energy. The second law, which we will explore later, describes the limitations in converting heat to work. In either case, pure thermodynamics has a different character from areas of physics that we have explored before because it deals only with macroscopic properties of systems. At some points, we will supplement the thermodynamics with its kinetic (i.e., statistical mechanical) interpretation; it is important to remember that although these methods are very related, they have significantly different logical underpinnings.

2 Ideal Gas Law

We are all familiar with the ideal gas law, $PV = nRT$. In pure thermodynamics, this law is developed from empirical considerations: it is direct consequence of the combination of Charles', Boyle's, Gay-Lussac's and Avagadro's laws. However, it is much more pleasing to embark on a study of thermodynamics with a firmer proof of the ideal gas law; for this, we must use statistical mechanics.

Consider the box shown in Figure 1. It is filled with particles of mass m all bouncing off the walls. We can determine the pressure by considering the momentum transfer when the particles collide elastically with the walls. Consider, to begin with, only the x direction; a representative particle shown in the diagram has a velocity with x -component u_x . Therefore, when it changes direction upon the collision, the impulse provided by the wall is $2mu_x$. The average time between collisions is simply $2L/u_x$. Therefore, the average force on the wall due to this particle is

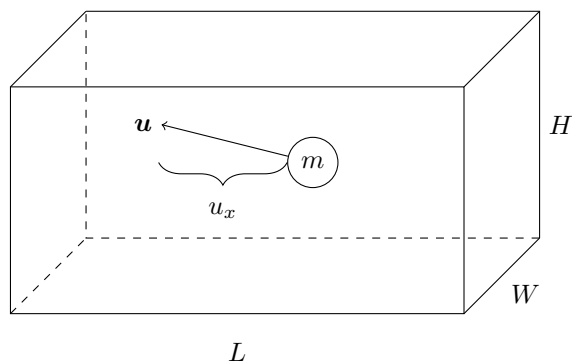


Figure 1: A rectangular box containing N particles of mass m .

$$F_x = \frac{2mu_x}{2L/u_x} = \frac{mu_x^2}{L}.$$

To find the pressure, we need to sum the forces from all the particles and divide by the area. To sum the forces, we can multiply N by the average force, and obtain finally

$$P_x = \frac{Nm\langle u_x^2 \rangle}{LWH} = \frac{Nm\langle u_x^2 \rangle}{V}.$$

Before moving on, we should extend this to three dimensions. We can simply replace $\langle u_x^2 \rangle$ by $\langle \mathbf{u}^2 \rangle$, but a particle free to move in three dimensions collides with a given wall only a third as often as if it were constrained to move in one dimension¹. Therefore, we have

$$PV = \frac{1}{3}Nm\langle \mathbf{u}^2 \rangle.$$

We recognize $m\langle \mathbf{u}^2 \rangle$ as twice the average kinetic energy. Since average kinetic energy is proportional to temperature, we can choose $\frac{2}{3}\langle E_k \rangle = kT$ and rewrite the equation as

$$PV = NkT.$$

Finally, we can substitute $N/N_a = n$ and $N_ak = R$ to obtain the familiar form of the ideal gas law,

$$PV = nRT.$$

Note that in this derivation we have chosen the Boltzmann constant k so that $\langle E_k \rangle = \frac{3}{2}kT$.

With the ideal gas law on firmer footing, we can investigate the simple situation of an isothermal transformation. We can see that if T is a constant, then PV is a constant. This is best illustrated on a pressure-volume or PV diagram, as in Figure 2.

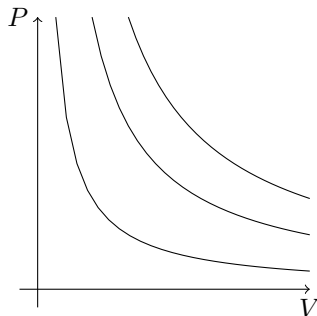


Figure 2: The hyperbolae on the PV diagram are isotherms.

When a gas expands, it does some amount of work on its surroundings. For a single particle, we know that $dW = \vec{F} \cdot d\vec{r}$; by dividing and multiplying by the area, and remembering that pressure is a normal force, we can translate this into $dW = P dV$. Therefore,

$$\begin{aligned} W &= \int_{V_1}^{V_2} P dV \\ &= \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= nRT \log \frac{V_2}{V_1} = nRT \log \frac{P_1}{P_2} \end{aligned}$$

¹This is a somewhat dubious argument. We can make all of this more rigorous by considering an arbitrary volume and doing some more calculus, but this method has the great advantage of simplicity.

We see that the work is simply the area under the curve on the PV diagram. This is true generally; in particular, for a cyclic process on a PV diagram traversed clockwise, the work is the area enclosed by the path on the PV diagram as shown in Figure 3.

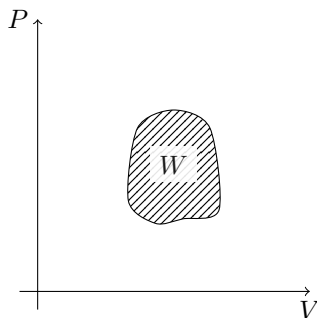


Figure 3: Cyclic processes perform work equal to the area they enclose on a PV diagram.

3 The First Law

In Thermodynamics, the first law is nothing but a statement of the conservation of energy. The essence of this lies in the fact that the change in energy of the system is the energy in minus the energy out. The energy in is what we define as heat: a source that transfers thermal energy to the system we are interested in. The responding “energy out” is the work that the system does: effectively, the system will respond to this change in energy by changing its configuration. A change in configuration requires work... so energy is expended due to the heat that is delivered. The total change in energy of the system is something that we call *Internal Energy*.

But what exactly is heat? To answer that, let us consider the definition of work

$$dW = -P_{ext} dV$$

Now we are being more specific. Yet we have to. We will define work as the work that the system does on its surroundings. Of course, a source of energy is added, and the system expands. It may seem as though the work occurs due to the expansion of the system itself. But, the expanding system is just an artifact of the heat that is added. However, the moment that there is an external pressure that is preventing the system from expanding, *then* the system does work in order to try to expand. It may not expand to its fullest potential because it loses energy while doing work on its surroundings, but that just follows from the above statement. The negative sign just means that the system loses energy as it does work on its surroundings. We’ll get to the weird slash symbol on the differential a bit later.

As heat is so commonly associated with temperature, we define

$$dq = c dT$$

Where c represents a heat capacity of the system: a variable that sort of depicts the tolerance of the system to the addition of thermal energy. The slash is here too... Now, we are ready to define the first law of thermodynamics. All this says is that

$$dU = dq + dW$$

Notice the plus sign is accounted for the fact that work is defined to be negative $P_{ext} dV$. But more importantly, notice how the internal energy of the system (U) does not have a slash... What’s up with that?

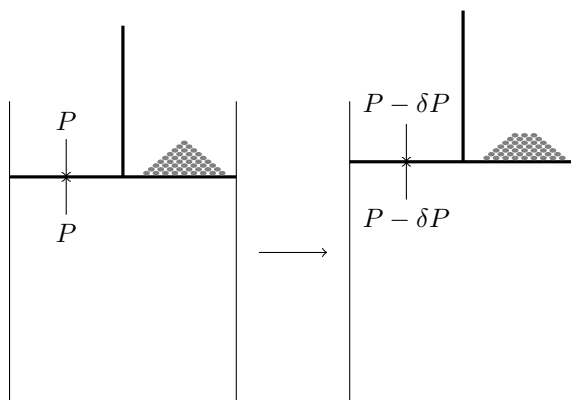


Figure 4: A process carried out quasistatically is reversible.

3.1 A Brief Excursion on Work

One of the most fatal flaws that people have is a misunderstanding of work is. For example, a system's internal pressure can be changing all it wants, but if it expands in a vacuum, it does NO work to its surroundings. How can its internal pressure change?... well, through an external source of heat, obviously. In fact, the evolution of the system is completely controlled by this external source: the motion of the object is not resisted in any way by external pressures that would otherwise quell it's energy by forcing it to do work. You may now ask the following pertinent question: the atmosphere is maintained at a steady and constant pressure... if a piston expands under this pressure, wouldn't the work done be the pressure times the change in its volume, regardless of the internal pressure. And of course, the answer is yes. The only way to truly produce the isothermal work proven in the previous section was if the process is done bit by bit, also called *quasistatically*.

As shown in the Figure 4, consider grains of fine sand placed on the piston. As one takes out sand, grain by grain, the weight of the piston (aka, the external pressure) will decrease. Now, each time a grain of sand is taken out, wait until the system stabilizes. This effectively forces the internal pressure to be equal to the external pressure. It is in THIS case, that the external pressure can be replaced by the internal pressure, thus completing the proof in the previous section.

What have we learned: consider external pressures, not internal. If a process is completed isothermally (slowly and in a heat bath), then we should expect to reverse the process (quasistatically), and get back to our original state. The ability of moving from one state to another without affecting their properties is known as *reversibility*. This is a fantastically important concept. Whenever you want to equate external and internal pressures, always think: is this process reversible? Is the word "slow" part of the problem statement?

4 Enthalpy

As many of you may know from chemistry, Enthalpy is the way we consider the heat of a particular reaction. Enthalpy is not quite heat...but the reason we equate this two quantities in chemistry is because most reactions take place under constant pressure conditions. We define Enthalpy H as

$$H \equiv U + pV$$

If we consider a small change in the enthalpy, we get

$$dH = dU + p dV + V dp$$

Substituting in the first law of thermodynamics, we get

$$dH = \bar{d}q + (p - p_{ext}) dV + V dp$$

Now, we will use the fact that the process is reversible. In this case, the second term drops, because the internal and external pressures are equalized. Then, if we consider our process to be that of constant pressure (known as *isobaric*), we get

$$dH = \bar{d}q$$

Thus, our results in chemistry are justified: we can consider the enthalpy change of a system to be the change in its heat, if the system is taken along a path of constant pressure. On the PV diagram, this path looks like a straight, horizontal line.

5 Thermodynamic States

We have kept using slashes. In this section we will see why. In multivariable calculus, we determined that a force is conservative and was able to determine a potential function. In a way, quantities like U , H , V , and P are such quantities, they do not depend on path. Thus, we can say that the loop integral of any of these quantities over a closed cycle is 0. Quantities like work or heat, however, do depend on path. Like friction, they are additive along the path that one travels, and do not return to their original value if one returns to his/her original position. We this indicate such inexact differentials with a slash.

If our differential is exact, we can represent them as a change in particular quantities we are familiar with. For $U(T, V)$, we can say

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (1)$$

For an ideal gas, the second term is zero, so we can almost always express U as a function of temperature only. For a non-ideal gas, the second term η_J can be quite large.

Similarly, we can make a similar claim about $H(T, p)$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad (2)$$

Again, the second term is zero (the partial derivative is denoted as μ_{JT} for a non-ideal gas) and we can thus express H only as a function of T .

6 Specific Heats

When energy is added to a substance, its temperature will increase. The rate at which this temperature increase occurs is called the specific heat, and varies between substances. There are actually two different values of the specific heat, depending on whether the gas is kept at constant pressure or at constant volume as heat is added. Let c_v and c_p be the specific heats at constant volume and constant pressure, respectively; we can determine expressions for both of them by manipulating the first law.

We will let $P dV$ be work done *by* the system (as opposed to work done *on* the system, which was our convention previously) so that we have for the first law:

$$dU + P dV = \bar{d}q,$$

we will replace the total differential dU with various expressions for it. First, choose T and V as independent variables, so that

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV.$$

Substituting this into the first law, we obtain

$$dq = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV.$$

If volume is held constant, then $dV = 0$. This gives us a simple expression for the ratio dq/dT at constant volume, which is of course just c_v :

$$c_v = \left(\frac{\partial U}{\partial T} \right)_V.$$

We can similarly take T and P to be the independent variables, this time also substituting a total differential for dV :

$$dq = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP.$$

When pressure is constant, $dP = 0$ and the first term of the right hand side gives us c_p :

$$c_p = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P.$$

This can be rewritten as

$$c_p = \left(\frac{\partial(U + PV)}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P$$

This is an important set of relationships: Internal Energy is related to the constant volume heat capacity as Enthalpy is related to the constant pressure heat capacity. It can be shown from kinetic theory that for an ideal monatomic gas,

$$\begin{aligned} c_v &= \frac{3}{2}R \\ c_p &= \frac{5}{2}R. \end{aligned}$$

Additionally, for ideal diatomic gases,

$$\begin{aligned} c_v &= \frac{5}{2}R \\ c_p &= \frac{7}{2}R. \end{aligned}$$

Note that in each case, $c_p = c_v + R$; one of the problems asks you to show that this relationship is always true.

The ratio K is defined to be c_p/c_v ; for monatomic gases $K = \frac{5}{3}$ and for diatomic gases $K = \frac{7}{5}$.

7 Adiabatic Processes

In an adiabatic process, the system does not exchange any heat with its environment. Therefore, $dq = 0$, which simplifies the first law significantly.

$$dU + dW = dU + P dV = 0$$

Now, we can substitute $dU = c_v dT$ to obtain²:

$$c_v dT + P dV = 0$$

²Note that we have tacitly assumed that U is a function of only T so that $c_v = \left(\frac{\partial U}{\partial T} \right)_V$ implies this relationship.

We can eliminate P with the ideal gas law; for the sake of simplicity, assume $n = 1$ so that $P = RT/V$:

$$c_v dT + \frac{RT}{V} dV = 0$$

$$\frac{dT}{T} + \frac{R}{c_v} \frac{dV}{V} = 0$$

$$\log T + \frac{R}{c_v} \log V = \text{const.}$$

$$TV^{\frac{R}{c_v}} = \text{const.}$$

Since $T = PV/R$, this can be written as

$$PV^{\frac{c_v+R}{c_v}} = \text{const.}$$

Using the result of problem 4, the exponent can be simplified to $\frac{c_p}{c_v} = K$, so

$$PV^K = \text{const.}$$

This is similar to the equation for an isothermal transformation, except for the exponent K . We saw previously that K is close to one, so that the adiabatic transformations are slightly steeper than the isothermal transformations on the PV diagram.

Take note of the assumptions that were made: an ideal gas, whose internal energy is only a function of temperature. Moreover, we assumed the process was reversible and quasistatic: indeed adiabatic process are more subtle. In fact, if we run the process too slowly, we risk heat leaking to our system. So an adiabatic process is defined as... not too fast that the process loses reversibility, but not too slow that the process loses adiabaticity.

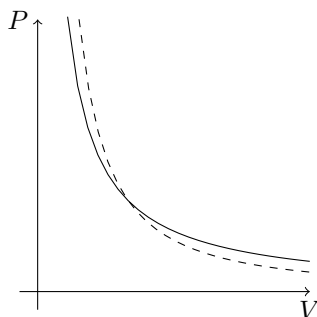


Figure 5: Adiabatic transformations are steeper than isothermal ones on the PV diagram.

8 Problems

1. Argue that a system does maximum work on its environment during a *reversible* process. You can show this by considering the “sand-graining” process to not be infinitesimally small.
2. As you may know, the ideal gas law is not a very good descriptor with more complex gases (hence its name). A more realistic approximation takes into account intermolecular forces and the relative size of the molecules (as compared to the mean free path between them).
 - (a). Argue why the pressure of the system will go up by the square of the molar density of the gas. The reasoning for the why the molar density goes down should be obvious (the space between the

molecules is reduced as their size is reduced)

(b) We can write this law in the new form $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$. Assume that one mole of gas expands in a reversible, isothermal process under the influence of this equation of state. Determine the work done by the gas on its surroundings, if it expands from a volume V_1 to V_2

(c) Assuming the joule coefficient of the gas is η_J , we know that a particular amount of heat must be delivered in order for the system to do work. Determine this heat input. Note that the internal energy is not a function of only temperature now.

3. (Semifinal 2008) A simple heat engine consists of a moveable piston in a cylinder filled with an ideal monatomic gas. Initially the gas in the cylinder is at a pressure P_0 and volume V_0 . The gas is slowly heated at constant volume. Once the pressure reaches $32P_0$ the piston is released, allowing the gas to expand so that no heat either enters or escapes the gas as the piston moves. Once the pressure has returned to P_0 the outside of the cylinder is cooled back to the original temperature, keeping the pressure constant. For the monatomic ideal gas you should assume that the molar heat capacity at constant volume is given by $C_V = \frac{3}{2}R$, where R is the ideal gas constant.

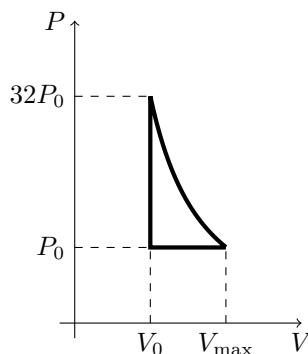


Figure 6: Problem 2

4. Prove that $c_p = c_v + R$ from the following analysis: consider the definition of c_p and c_v . Using the equation that related enthalpy and internal energy, differentiate both sides by T . One partial derivative is non-trivial, but it can be dealt with by using the fact that $\left(\frac{\partial U}{\partial V}\right)_T = 0$.
5. When air rises from the surface of the Earth, it expands and cools. Assuming this process is adiabatic, find the rate of cooling of air with respect to height. Assuming that air is a diatomic gas with molar mass 28.9 grams, you should obtain a decrease of 9.8 degrees per kilometer.
6. The isothermal compressibility κ for a gas is defined as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.$$

For an ideal gas, it is easy to see that $\kappa = \frac{1}{P}$. Find the isothermal compressibility of a van der Waals gas.