

# Thermodynamics

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Thermodynamics is a very different branch of physics from mechanics that deals with looking at macroscopic properties of systems in order to describe heat as another form of energy and describe its transfer. For a system of many particles that transfer heat, it is much less useful to set up many equations of motion for each individual particle and track its energy, so we will appeal to statistical mechanics and looking at quantities that are more useful for describing large systems.

## 1 Conventions and Setups

Inside a system with many particles, we will use the *pressure*  $p$  that these particles exert on the boundary of the system (or the force per unit area), the *volume*  $V$  of the system, and the temperature  $T$ . Temperature is a rather poorly defined concept - other than the obvious definition that it measures "hotness" or "coldness," we more or less have to arbitrarily construct the absolute temperature system that we use (currently, it is based off fixing the value of the Boltzmann constant,  $k$ , that we will discuss later).

Frequently we will use PV diagrams, with volume on the horizontal axis and pressure on the vertical axis to describe the state of a thermodynamic system. Paths drawn between two points will describe thermodynamic processes.

It will be important for us to distinguish between reversible processes and irreversible processes. If we can transform a system from state A to state B by slowly altering the variables of the environment, if we can do the same in reverse, we may reverse the transformation. (We won't see many examples of irreversible processes early on, but certainly they will be important in our discussions later).

As we deal with heat as another form of energy to be accounted for, let us clarify some of the quantities that we will be working with. We will often deal with the work done *by the system on its surroundings as positive* and represented by  $W$ , the internal energy (the kinetic energy of the particles within)  $U$ , and the heat transferred to and from the system  $Q$ .

We will encounter processes that leave one of these variables constant. If volume is held constant, or no work is done by the system, we call the process *isochoric*; if temperature is held constant, we call the process *isothermic*; if pressure is held constant, we call the process *isobaric*; and if no heat is transferred in or out of the system, we call the process *adiabatic*.

Just with this, we can actually relate the work done by the system  $W$  to its internal variables. Recall that  $dW = \vec{F} \cdot d\vec{r}$ . For a small expansion of the system normal to the walls of the system, we have  $dV = A dr$  and  $p = \frac{F}{A}$ , we have  $dW = p dV$ . For a system changing in volume, the work done by the system on its surroundings is:

$$W = \int_{V_1}^{V_2} p dV$$

On a PV diagram, this is merely the area underneath the curve moving from one state to another with respect to the horizontal axis. If the curve happens to be a loop (so the process is a cycle) the work done is simply the area of the loop (if the loop is traversed clockwise).

## 2 The Ideal Gas Law

We will appeal to statistical mechanics to derive the Ideal Gas Law.

Let us consider a collection of idealized gas particles of mass  $m$  and speed  $v$  in a box, assuming the motion of these small particles is random and not influenced by forces between the particles. Let us assume that there are  $N$  particles in the system. and the uniform density of particles is  $n = \frac{N}{V}$ . We want to consider the pressure on one side of the box if it has area  $A$ .

Consider a particle with speed in the  $x$ -direction  $v_x$ . that collides elastically with the side of the box. We can see that after the collision, the particle reverses direction, so the particle imparts an impulse  $2mv_x$  to the side. In a time  $\Delta t$ , only particles that are close enough to the side of the box will deliver impulse. These particles occupy the volume  $A \cdot v_x \Delta t$  closest to the side of the box, so the number of particles that hit the side of the box in this time is  $nAv_x \Delta t$ . We can compute the force and pressure on the side of the box:

$$F = 2mnAv_x^2 \quad P = 2nmv_x^2$$

Up until this point, we have been assuming that all the particles have the same velocity. This is not true - they all move in different directions. We have to take the average of the velocities - or rather, the average squared velocity to find the pressure:

$$P = nm \langle v_x^2 \rangle$$

We lose a factor of 2 from our original expression because in a volume, we expect half of them to be moving towards the side of the box, and half moving away - so really, the density of particles moving towards the side of the box is  $\frac{n}{2}$ .

We chose  $x$  arbitrarily, but we have three linearly independent directions in this volume, none of which that are particularly special. In the  $x$ -,  $y$ -, and  $z$ -directions, we have that these average velocities squared are the same:

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

We would like to write this in terms of the overall average velocity (squared),  $\langle v^2 \rangle$ , using linearity of expectation:

$$\langle v^2 \rangle = \langle v_x^2 + v_y^2 + v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

Therefore, the pressure on the side of the box is:

$$P = \frac{1}{3}nm \langle v^2 \rangle = \frac{2}{3}n \left\langle \frac{1}{2}mv^2 \right\rangle$$

This final rearrangement gives us the average kinetic energy of the particles as a term. If we multiply through by the volume:

$$PV = \frac{2}{3}nV \left\langle \frac{1}{2}mv^2 \right\rangle = \frac{2}{3}N \left\langle \frac{1}{2}mv^2 \right\rangle = \frac{2}{3}U$$

It is natural to define the average kinetic energy of the particles multiplied by number of particles as the total internal energy of the system,  $U$ . This gives us half of the ideal gas law. Before we argue the second half, it's worth noting that we may more generally write this as:

$$PV = (K - 1)U$$

where for a monatomic gas,  $K = \frac{5}{3}$ .

We will now make a somewhat wishy-washy argument that the internal energy  $U$  is proportional to the temperature  $T$  by showing that they must be proportional at an equilibrium between two systems. From experiment, we are aware that two systems at different temperatures that can transfer heat between these systems will eventually settle down to have the same temperature. We may argue that the same is true of internal energy. Suppose these two systems were in contact with each other and separated by a sliding boundary. We may argue that the velocity of the boundary can be modeled as the velocity of the center of mass of a new system of a particle from each system colliding with each other with the average velocities of particles in the two systems. In this case, since energy and momentum are conserved, the momenta of these particles simply change direction. At equilibrium, where the boundary does not move, it must then be true that the particles must have the same kinetic energy, as the energy is conserved. This establishes that  $\langle KE \rangle = \frac{3}{2}kT$ , for well-chosen  $k$  (the extra  $\frac{3}{2}$  is more-or-less arbitrary).  $k$  in this case is called the *Boltzmann* constant. This gives

$$U = \frac{3}{2}NkT$$

Plugging this in to our earlier derived expression, we have that

$$PV = NkT$$

and if we wish to express this in terms of moles of gas, defining the ideal gas constant  $R$  to be  $k \cdot N_A$ , where  $N_A$  is Avogadro's constant, we have the familiar

$$PV = nRT$$

if  $n$  is the number of moles of gas, usually taken to be 1. A similar substitution (assuming  $n = 1$ ) also gives us, for an ideal gas

$$U = \frac{3}{2}RT$$

We will frequently make use of these results involving ideal gases when discussing them in a system.

### 3 The First Law of Thermodynamics

The first law of thermodynamics is essentially a statement of the conservation of energy. Any change in the internal energy system can be attributed to a change in heat or work done by the system:

$$dU = \delta Q - \delta W$$

The change in the work is negative, because we define  $W$  to be the work done by the system. If  $dW$  is negative (work is done to the system), and no heat is added,  $dU$  will be positive.

Note the use of the  $\delta$ s. This is used to indicate that the values of these quantities are path-dependent on a PV diagram. On a loop on a PV diagram, integrating along this path will not produce zero in general for quantities such as  $Q$  and  $W$ , whereas it definitely will for  $U, p, V, T$ . Using these  $\delta$ s indicates these differentials are *inexact*, whereas for these path-independent quantities we can use the same exact differentials that we're used to.

For a system, one useful quantity to know is the heat capacity, or thermal capacity of the system,  $C$ , depending on whether the system is being heated at constant volume or constant pressure. We define it as

$$C = \frac{\delta Q}{dT}$$

We can derive explicit relations for the heat capacities at constant volume and pressure using the first law of thermodynamics. First, we will assume that the internal energy  $U$  is a function of temperature and either pressure or volume, depending on what we choose to compute.

$$U = U(T, p) : \quad dU = \left( \frac{\partial U}{\partial p} \right)_T dp + \left( \frac{\partial U}{\partial T} \right)_p dT$$

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

If we write the first law in the form  $dU = \delta Q - p dV$ , we can write  $\delta Q$  in the following ways:

$$\delta Q = \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] dV + \left( \frac{\partial U}{\partial T} \right)_V dT$$

$$\delta Q = \left[ \left( \frac{\partial U}{\partial p} \right)_T + p \left( \frac{\partial V}{\partial p} \right)_T \right] dp + \left[ \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p \right] dT$$

Notice this gives

$$C_V = \left( \frac{\delta Q}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V \quad C_p = \left( \frac{\delta Q}{dT} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p$$

For an ideal gas, we already have shown that  $U$  is only dependent on  $T$ , so we have  $\left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_p = \frac{dU}{dT}$ . This directly gives

$$C_p = C_V + p \left( \frac{\partial V}{\partial T} \right)_p = C_V + p \cdot \frac{R}{p} = C_V + R$$

In general, for an idealized gas, recall we defined a constant  $K$  such that  $PV = (K - 1)U$ . The same constant shows up here - in fact,  $K$  is defined to be  $\frac{C_p}{C_V}$ . From actually computing  $\frac{dU}{dT}$ , we can show that

$$K - 1 = \frac{R}{C_V}$$

With this, we can look at what happens to an ideal gas undergoing an adiabatic transformation (other transformations are not super difficult to look at). From the definition of  $C_V$ , we can note that  $dU = C_V dT$  and  $\delta W = p dV$ . Adiabatic transformations have  $\delta Q = 0$ , so this gives:

$$C_V dT = -p dV$$

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

$$\frac{1}{T} dT + \frac{R}{C_V} \cdot \frac{1}{V} dV = 0$$

Integrating, we have, for some constant  $D$ :

$$\ln T + \frac{R}{C_V} \ln V = D$$

$$TV^{K-1} = D$$

$$PV^K = D$$

This is a very useful result for ideal gases - it's very similar to the relation between pressure and volume for isothermal transformations. In particular, it's good to remember for monatomic gases, we have  $PV^{\frac{5}{3}}$  is constant for adiabatic transformations.

In practice, achieving an adiabatic transformation is subtle - we cannot do the transformation slowly, or heat will leak from the system. At the same time, however, in order to use the formula for work that we used (using internal pressure), we must force the internal pressure to be equal to the pressure of the surroundings,

which can only be done quasistatically (in chunks) and slowly, so that it is reversible.

## 4 The Second Law of Thermodynamics

We will state the second law of thermodynamics in two different ways through the following two statements, *Kelvin's Postulate* and *Clausius' Postulate*.

**Kelvin's Postulate.** It is impossible for a transformation of a system to only involve the removal of heat to do the same amount of work on the surroundings and no other changes.

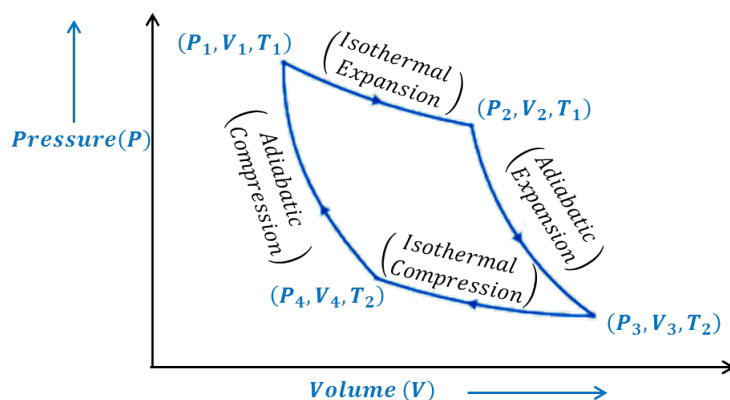
**Clausius' Postulate.** It is impossible for a transformation to move heat from a colder body to a hotter body without doing work.

In order to show that these are equivalent statements, we will show a violation of Kelvin's Postulate will give a violation of Clausius' Postulate and vice versa. This will show that these statements are equivalent. Suppose we could extract heat from a system with temperature  $T_1$ , and convert it fully into work, in violation of Kelvin's Postulate. Then, we could convert this work back into heat by means of friction and raise the temperature of another body with temperature  $T_2$  with this heat. We could do this arbitrarily many times - thus, at some point, once  $T_2 > T_1$ , we will be moving heat from a colder body to a hotter body without doing work. This is a violation of Clausius' Postulate, as desired.

To show the reverse, we will need to discuss heat engines, and in particular, the Carnot cycle, to easily prove Clausius' Postulate is equivalent to Kelvin's Postulate.

### 4.1 Heat Engines and the Carnot Cycle

We will construct an idealized machine that uses heat to do work. This particular example is called a Carnot cycle, but of course there are other varieties and ways to do work using heat. This is just the classical example.



From the state 1 on the PV diagram (with corresponding indices), we will first allow the system to expand isothermally by slowly increasing the volume and decreasing the pressure, thus preserving the temperature of the system to reach state 2. We will then expand the system adiabatically, by insulating the system from heat, and then allowing the pressure to decrease further and the volume to increase a little more to reach state 3. This also decreases the temperature of the system. Now, we will decrease the volume and increase

the pressure, making the system contract isothermically, until it reaches state 4. In order to go back to state 1, we will finally insulate the system from heat, slowly decrease the volume and increase the pressure, making the system increase in temperature but contract adiabatically until it returns to the original state.

By the first law, the work done by this cycle on the surroundings is the net heat gained by the system. If the system gained heat  $Q_2$  while it was expanding isothermically, and lost heat  $Q_1$  while contracting, the work  $W$  done is  $Q_2 - Q_1$ . This is the amount of useful work done by the system - the rest is lost to some external source as heat. With this in mind, we can define the efficiency  $\eta$  as the work performed by the system to the total heat gained:

$$\eta = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

Since we explicitly did all of these processes slowly, we can also reverse the cycle to give up a net amount of heat so work can be done to it.

With this in mind, we can now show if Clausius' Postulate is violated, so will Kelvin's Postulate be violated. Suppose we were able to transfer heat from a colder source to a hotter one ( $T_2$  to  $T_1$  in the diagram above) without doing work and not changing the temperatures of the sources. This could be accomplished by running our Carnot cycle in reverse, removing heat from the colder source that is transferred to the hotter source, but this requires that work be done to the hotter source by the first law. This means that the colder source has lost heat to do work on an external body, without changing any other variables - which is a violation of Kelvin's Postulate.

The Carnot cycle is also useful as it is useful for thought experiments involving reversibility. In fact, Carnot proved the Carnot cycle operating between two temperature sources is the most efficient, and the efficiency depends only on the temperatures of the sources in the following way:

$$\eta = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

These two expressions for the efficiency can be rearranged to show

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

If we were to transfer an infinitesimal amount of heat between the heat sources, it would appear to be useful to define a quantity  $S$  such that

$$dS = \frac{\delta Q_{rev}}{T}$$

Around the whole Carnot cycle, the quantity  $S$  would be unchanged. It turns out for any reversible path,  $S$  is constant - and we refer to  $S$  as the entropy. From here, we can present the traditional statement of the second law of thermodynamics - that the entropy of a system can only increase or stay the same - as the entropy change of an irreversible process is always positive, and zero if the process is reversible.