

First Law and Work

RUBAIYA EMRAN, BRYAN LU

August 23, 2019

1 Introduction

Thermodynamics deals with the relations and transformations between heat and other forms of energy, especially mechanical work. Unlike classical mechanics, it considers macroscopic properties of systems consisting of many particles in which it is impractical to set up equations of motion for each individual particle. The first law of thermodynamics, which is discussed here, shows how work and heat relate through the conservation of energy. The laws of thermodynamics can be understood through a kinetic interpretation based on statistical mechanics, which describes the behavior of large ensembles of particles.

2 Setup

We describe our thermodynamics systems using the pressure P , volume V , and temperature T . These are average properties of the macroscopic systems, as we do not care about the motions of each individual particle but rather the macroscopic behavior.

We characterize the geometry of the system purely using the volume. The majority of thermodynamical properties are independent of shape, so volume is the only geometric quantity given. For high surface area cases, this assumption breaks down - the surface area must also be considered.

Given a certain amount of the substance contained in a system, the volume, temperature, and pressure are not independent quantities. Instead, they are connected by an *equation of state* of the form

$$f(P, V, T) = 0.$$

This equation depends on the properties of the substance of which the systems consists. For example, for an ideal gas, the equation of state is the *ideal gas law*

$$PV = nRT.$$

We typically use PV diagrams to represent a thermodynamic system. Volume is on the horizontal axis and pressure is on the vertical, and a point on the plane defines the state of the system. Thermodynamic processes are represented by curves drawn between two points.

There are two main classes of transformations: *reversible* and *irreversible*. A reversible transformation takes place when the external conditions are changed so slowly that the system has time to adjust to equilibrium during each step of the transformation. Reversible transformations can, as the name suggests, be reversed by realizing the opposite sequence of steps. When the intermediate states are not states of equilibrium, the transformation is irreversible.

During a transformation, we define W to be the work done by the system on its surroundings. W is positive if the system has performed work on its surroundings and negative if the surroundings have performed work on the system. We can relate this quantity to the internal variables of the system. We know that $dW = \vec{F} \cdot d\vec{r}$. If we imagine expanding the system normal to its walls, we have $dV = A dr$ and $P = \frac{F}{A}$, so $dW = PdV$. In general, we then have that

$$W = \int_{V_1}^{V_2} PdV. \quad (1)$$

This is the area beneath the curve connecting one state to another. If the curve is a loop, the work done is the area of the loop if the loop is traversed clockwise.

Finally, we define several special types of transformations. If volume is held constant, the process is *isochoric*; if temperature is constant, it is *isothermic*; if pressure is constant, it is *isobaric*; and if no heat is transferred in or out of the system, it is *adiabatic*.

3 Ideal Gas Law

We now derive the equation of state for an ideal gas. Consider a collection of ideal gas particles of mass m and speed v in a box, and assume the motion of these particles is random, meaning that the forces between the particles are negligible. Let there be N particles in the system, and let the density of particles be $n = \frac{N}{V}$.

We now calculate the pressure on a side of the box with area A . Consider a particle with speed v_x in the x -direction that collides elastically with the wall of the box. The particle reverses direction after the collision, so it imparts an impulse $2mv_x$ on the wall. In a time Δt , only particles close enough to the wall will deliver an impulse. These particles occupy a volume $Av_x\Delta t$, so the number of particles that hit the side of the box is $nAv_x\Delta t$. Then the force is

$$F = 2mnAv_x^2,$$

so

$$P = nmv_x^2.$$

The above expression assumes that all particles have the same velocity. However, as they all move in different directions, and only about half of them will be moving towards the side of the box, we have

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

Of course, we have three linearly independent directions in the volume, none of which is particularly unique. We assume therefore that

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle,$$

where $\langle v^2 \rangle$ is the overall average squared velocity. Then

$$PV = \frac{1}{3}nm \langle v^2 \rangle V = \frac{2}{3}N \left\langle \frac{1}{2}mv^2 \right\rangle = \frac{2}{3}U,$$

where U is the *internal energy* of the system (that is, the kinetic energy of the particles within the system).

We note that, more generally, we define K such that

$$PV = (K - 1)U. \quad (2)$$

As shown here, $K = \frac{5}{3}$ for a monatomic gas.

Intuitively, the internal energy U is proportional to the temperature T . We can show 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 to each other 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 the average kinetic energy is proportional to the temperature at an equilibrium between two systems. We then define k such that $\langle KE \rangle = \frac{3}{2}kT$. In this case, k 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

$$PV = nRT, \tag{3}$$

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

$$U = \frac{3}{2}RT. \tag{4}$$

Equations 3 and 4 will be useful for problems involving ideal gases.

4 First Law of Thermodynamics

The first law of thermodynamics is a statement of the conservation of energy. It states that any change in the internal energy of the system must be caused by a change in heat or work done by the system:

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

Note that W is negative here because it is the work done *by the system on the surroundings*. We use the δ s to denote that these quantities are path-dependent on a PV diagram.

We now define the heat capacity, or thermal capacity, of system as

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

There are different heat capacities at constant volume and pressure.

At constant volume, we write U as a function of V and T (recalling that T , P , and V are not independent), so $U = U(T, V)$. Then

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

The first law gives

$$\delta Q = dU + PdV = \left(\frac{\partial U}{\partial T} \right)_V dT,$$

so

$$C_V = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_V.$$

When pressure is held constant, we instead write $U = U(P, T)$. Then

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

By the first law,

$$\delta Q = dU + PdV = dU + P \left[\left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \right] = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT$$

so

$$C_P = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P.$$

For an ideal gas,

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V = \frac{dU}{dT},$$

so

$$C_P = C_V + P \left(\frac{\partial V}{\partial T} \right)_P = C_V + R.$$

We find also that

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

where K is defined in equation 2.

With this background, we can now consider ideal gases undergoing adiabatic transformations. We specifically study these because the other transformations are comparatively easy to analyze. Adiabatic transformations have $\delta Q = 0$, so

$$\begin{aligned} C_V dT &= -PdV, \\ C_V dT &= -\frac{RT}{V} dV, \\ \frac{dT}{T} &= \frac{R}{C_V} \frac{dV}{V}. \end{aligned}$$

Integrating both sides, we have

$$\ln \left(\frac{T}{T_0} \right) = \frac{R}{C_V} \ln \left(\frac{V}{V_0} \right).$$

This means that

$$TV^{K-1} = PV^K = D \tag{5}$$

for some constant D during adiabatic transformations for ideal gases. For monatomic gases, equation 5 implies that $PV^{\frac{5}{3}}$ is constant during adiabatic transformations.

5 Problems

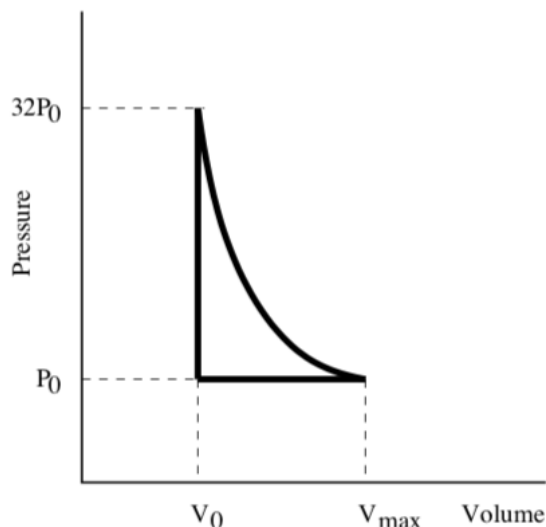
1. Single bubble sonoluminescence occurs when sound waves cause a bubble suspended in a fluid to collapse so that the gas trapped inside increases in temperature enough to emit light. The bubble actually undergoes a series of expansions and collapses caused by the sound wave pressure variations. We now consider a simplified model of a bubble undergoing sonoluminescence. Assume the bubble is originally at atmospheric pressure $P_0 = 101$ kPa. When the pressure in the fluid surrounding the bubble is decreased, the bubble expands isothermally to a radius of $36.0 \mu\text{m}$. When the pressure

increases again, the bubble collapses to a radius of $4.50\ \mu\text{m}$ so quickly that no heat can escape. Between the collapse and subsequent expansion, the bubble undergoes isochoric (constant volume) cooling back to its original pressure and temperature. For a bubble containing a monatomic gas, suspended in water of $T = 293\ \text{K}$, find

- the number of moles of gas in the bubble,
- the pressure after the expansion,
- the pressure after collapse,
- the temperature after the collapse, and
- the total work done on the bubble during the whole process.

You may find the following useful: the specific heat capacity at constant volume is $C_V = \frac{3}{2}R$ and the ratio of specific heat at constant pressure to constant volume is $\gamma = \frac{5}{3}$ for a monatomic gas.

- 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. You may express your answers in fractional form or as decimals. If you choose decimals, keep three significant figures in your calculations. The diagram below is not necessarily drawn to scale.



- Let V_{max} be the maximum volume achieved by the gas during the cycle. What is V_{max} in terms of V_0 ? If you are unable to solve this part of the problem, you may express your answers to the remaining parts in terms of V_{max} without further loss of points.
- In terms of P_0 and V_0 determine the heat added to the gas during a complete cycle.
- In terms of P_0 and V_0 determine the heat removed from the gas during a complete cycle.
- What is the efficiency of this cycle?