

Chapter 11

Temperature and Heat

11.1 Temperature Scales

In the previous chapter, we were discussing one of the wonderful measuring devices humans and many animals come equipped with, the ear. In this section, we will discuss another of these natural sensors we routinely employ to give us a sense of the state of our surroundings. All are aware of the feeling of hot or cold. That is, through our skin, and even our body as a whole, we receive sensations we refer to as cold, cool, warm and even hot. Even without knowing any of the physical details behind the phenomenon we are able to conclude that this sensation is somehow associated with matter around us. For example, the air is cold, the object is hot and so forth. This phenomenon is so common and important that humans have developed scales in order to quantify the effect. We refer to a value obtained from a measurement, using one of these scales, as a *temperature*. These measurement systems are therefore called *temperature scales*.

Here we will discuss three well-known temperature scales, Fahrenheit, Celsius and Kelvin. One of the most obvious events in nature, associated with temperature, is the freezing of water. It is no surprise then that two of these scales are directly connected with this occurrence. Assume that we somehow have a device that measures temperature. A device that measures temperature is referred to as a *thermometer*. How a thermometer can be built will be discussed later.

The freezing (or melting) point of water, at atmospheric pressure, is defined to be at the temperature of 32 on the *Fahrenheit scale*. As per tradition, this measurement value is referred to as 32 degrees Fahrenheit or simply 32 °F. Also on this scale the boiling point for water, at atmospheric pressure, is defined to be 212 °F. So you can see that on this scale you have 180 intervals or degrees between the melting point and boiling point of water. Fahrenheit is a temperature scale still in use in North America. It has a nice human feel to it; ~100 °F is the point where temperatures get a bit too hot for the human body both inside and out!

The *Celsius scale* is a convenient temperature scale that is in widespread use throughout the world. On this scale, the melting point for water, at atmospheric pressure, is set to be zero, or 0 °C. Also the boiling point for water, at atmospheric pressure, is defined to be 100 °C. So we see that there are 100 degrees or intervals on this scale between the melting and

boiling point of water.

With such scales in mind, how would one make a device that measured temperature? Most pure materials will expand when undergoing a temperature increase, a phenomenon we will discuss in a subsequent section. Suppose you had a certain mass of pure liquid. When the temperature of the sample is increased the mass remains constant but typically the density does not. Therefore, the volume of the sample changes. The volume change versus temperature for many pure samples, at atmospheric pressure, is well known. Therefore, since the volume of the sample changes in a predictable fashion, as temperature changes, one can use this material to determine the temperature. For example the volume of the sample is known at 0 °C and then also at 100 °C. The intermediate values for the volume of the sample can be used to determine temperature between these two values and even above and below them. Alcohol and mercury thermometers exploit this effect. As will be discussed later, there are many other properties in pure materials aside from density, that vary in a regular fashion due to changes in temperature. Many of these temperature dependent changes can be used to develop temperature measuring devices.

The French scientist Jacques Charles (1746-1823) studied how changing temperatures affected the properties of gases. He found that at constant pressure the volume of a gas would decrease in a regular fashion with decreasing temperature. Though there was a limit to how low the temperature for his experiment could be set, it was found that if the volume versus temperature data were extrapolated to zero volume it converged towards the temperature of approximately -273 °C. Since that time thermodynamicists (people who use the laws of thermodynamics to investigate the thermal properties of matter) have declared that this point is the *absolute zero* for temperature. That is, it seems to be that nature itself has declared a minimum possible value for temperature. This value is now taken to be -273.15 °C.

A temperature scale that has its zero point at absolute zero is the *Kelvin scale*. On this scale absolute zero is set to be zero Kelvin or simply 0 K. The Kelvin is the SI unit for temperature. So, we have that 0 K = -273.15 °C. An interval or degree on the Kelvin scale is equivalent to one on the Celsius scale. The temperature scale used in most scientific work is the Kelvin scale.

It is useful to be able to convert between the three scales. However, since they all have different zero points we cannot use a conversion factor as has been the case previously with units conversions. We need a formula for conversion in this case. The simplest one to write is for the transition from temperature in Kelvin, T_K , to Celsius, T_C :

$$T_C^\circ = T_K - 273.15 . \quad (11.1)$$

Example 11.1

Derive a formula for converting from temperature in degrees Fahrenheit to Celsius.

Let the temperature in Celsius be given by T_C and Fahrenheit by T_F . We assume a linear relationship between the two so that the conversion formula is of the form

$$T_C = mT_F + b .$$

Let's find values for the constants m and b . At 0 °C, it must be that the Fahrenheit temperature is 32 °F so that

$$0 = 32m + b \quad (\text{i}).$$

Also, at 100 °C it must be that the Fahrenheit temperature is 212 °F. This leads to

$$100 = 212m + b \quad (\text{ii}).$$

solving Eq. (i) for m and Eq. (ii) for b gives

$$m = -\frac{b}{32} .$$

$$b = 100 - 212m .$$

Eliminating by substitution in Eq. (ii) yields

$$100 = -\frac{212b}{32} + b$$

Solving this for b we get

$$b = -\frac{32(5)}{9} .$$

Inserting this result for b into Eq. (i) leads to $m = 5/9$ so that

$$T_C = \frac{5}{9}T_F - \frac{32(5)}{9} .$$

Factoring out the common factor of 5/9 gives the final result:

$$T_C = \frac{5}{9} (T_F - 32) .$$

11.2 Thermal Expansion

It was mentioned, in the previous section, how material properties that vary with temperature can be used to create devices that measure temperature. Pure materials in most states, solid, liquid and gas, will expand when their temperature is increased. In this section the expansion or contraction of a pure solid or liquid, due to a change in temperature, will be considered.

It is convenient to consider a thin rod of the solid material of interest. If the length of the rod at some reference temperature, T_o , is l_o then with an increase in temperature, ΔT , the length of the rod will increase by the amount Δl .

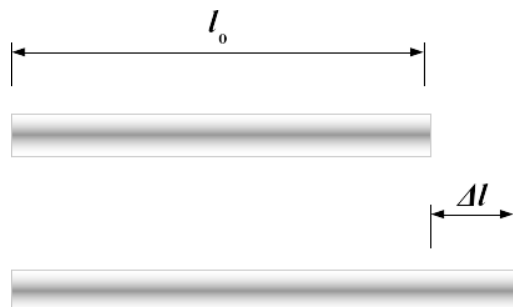


Figure 11.1: A rod of length l_0 at temperature T_0 increases by the length Δl with increase in temperature, ΔT .

It is known from experiment that in many cases $\Delta l \propto l_0 \Delta T$. An equality can then be written by introducing the constant α , the *linear expansion coefficient*.

$$\Delta l = \alpha l_0 \Delta T. \quad (11.2)$$

Linear expansion coefficients for a variety of pure materials are listed in Table 11.1.

Table 11.1: Linear expansion coefficients at room temperature (25 °C).

Metals	
Substance	(10^{-6} K^{-1})
Aluminum	23.1
Copper	16.5
Gold	14.2
Iron	11.8
Lead	28.9
Nickel	13.4
Platinum	8.8
Silver	18.9
Semiconductors (Ceramics)	
Substance	(10^{-6} K^{-1})
Silicon	2.6
Germanium	5.8
Carbon (Diamond)	1.18

Example 11.2

A thin silver rod of 0.500 mm in length is connected on one end to a copper rod of 0.250 mm in length. Both rods are initially at 25 °C. If the temperature surrounding the composite rod is raised to 525.0 °C what is the new overall length of the rod?

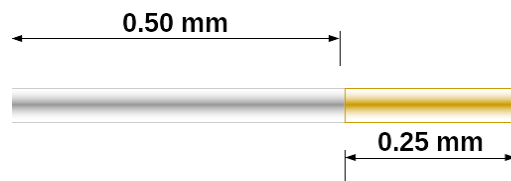


Figure 11.2: A composite rod of silver and copper.

Using the coefficients of linear expansion from Table 11.1, we compute the change in length for each material and then add to get the total increase in length and thus the total length.

For the silver section we get

$$\Delta l_{Ag} = (18.9 \times 10^{-6})(0.5 \times 10^{-3})(525 - 25) \approx 4.73 \times 10^{-6} \text{ m} .$$

For the copper section

$$\Delta l_{Cu} = (16.5 \times 10^{-6})(0.25 \times 10^{-3})(525 - 25) \approx 2.06 \times 10^{-6} \text{ m} .$$

So the new total length will be

$$0.500 \times 10^{-3} + 0.250 \times 10^{-3} + 4.73 \times 10^{-6} + 2.06 \times 10^{-6} = 0.757 \text{ mm} .$$

It is also a fact that most liquids expand with increasing temperature. However, the idea of a linear expansion is not useful when dealing with liquids. We would rather consider the expansion of the volume as a whole. Let the volume of a liquid at a known temperature be V_o . It is known from experiment that when a liquid undergoes a change in temperature ΔT_o , it will undergo a change in volume ΔV such that $\Delta V \propto V_o \Delta T$. We introduce a constant, β , referred to as the *the coefficient of volume expansion* so we have that

$$\Delta V = \beta V_o \Delta T . \quad (11.3)$$

Values for the coefficient of volume expansion, for selected liquids, are listed in Table 11.2.

Table 11.2: Volume expansion coefficients for liquids at 20 °C.

Substance	(10^{-6} K^{-1})
Water	210
Ethanol	1120
Mercury	182
Benzene	1240
Octane	720
Glycerine	540

11.3 Thermal Properties of Gases

For the physical scientist, it is desirable to be able to relate a physical property, such as the sensation of hot or cold (temperature), to some other physical process that is understood. One possible approach is to connect this phenomenon to activity at the atomic level in the sample. This method of description will be considered later in this chapter. For now, we want to concentrate on the thermal properties of gases without any discussion of activity at the atomic level.

Suppose there is a gas enclosed in a fixed cylinder with a movable piston. Being interested in the thermal properties of the gas we might want to know at any given time the amount, or mass m , of gas present, the volume, V , occupied by the gas, the pressure, P , of the gas and its temperature T . These quantities tell us something about the physical state of the gas at any given time therefore, they are referred to as *state variables*.

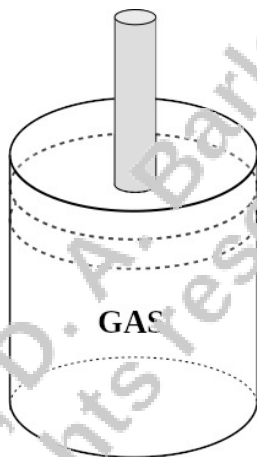


Figure 11.3: A cylinder containing a gas with a movable piston.

For the study of gases it is often more convenient to consider the number of particles present rather than their mass. By particle here, it is meant an atom or some stable combination of atoms, a *molecule*. To track the number of particles in the gas, we use the concept of a *mole*. A mole is a certain number of things like a dozen. $1 \text{ mole} = 6.02 \times 10^{23}$ items. It is, relatively speaking, a very large number of things but when dealing with small entities such as atoms, or molecules, this is a rather convenient number.

A mathematical relationship between the state variables, P, V, T and number of moles n , for a given gas, would be very useful to know. We call such an expression an *equation of state*. The results of several famous experiments carried out on gases beginning in the 17th century, can be used to assemble a simple, yet famous, equation of state.

The first of these to consider is a result due to Robert Boyle (1627-1691). In all cases here let us assume that the experiment was carried out for a gas in a cylinder with a movable piston as depicted in Fig. 11.3. Boyle found that if the number of moles and the temperature of the gas are held constant, then its volume is inversely proportional to its pressure; a result now referred to as *Boyle's Law*.

$$V \propto \frac{1}{P}, \quad \text{Boyle's Law .} \quad (11.4)$$

One could at this point introduce a constant of proportionality and have a useful relationship between P and V but only valid for cases of constant temperature T . Instead, let us consider the results of two other famous experiments that will allow us to write an equation of state which would also involve the effects of changing temperature.

The first of these is the result due to Jacques Charles which was discussed previously when dealing with temperature scales. He found that for situations of constant mole number and pressure that the volume of a gas is directly proportional to its temperature; a result now known as *Charles' Law*.

$$V \propto T, \quad \text{Charles' Law .} \quad (11.5)$$

Finally, Joseph Gay-Lussac (1778-1850) found that for a gas at constant volume and mole number the pressure is directly proportional to the temperature; a result now referred to as *Gay-Lussac's Law*.

$$P \propto T, \quad \text{Gay-Lussac's Law} \quad (11.6)$$

Though it goes by no special name, it is also well established that the amount of gas present has an effect upon its volume and pressure. In view of Charles' and Gay-Lussac's laws this can be stated as

$$PV \propto nT. \quad (11.7)$$

Eqs. (11.4) through (11.7) can be combined using a single constant of proportionality as

$$PV = nRT, \quad (11.8)$$

where the constant R is called *the gas constant*. The above experiments show that $R = 8.314$ J/(mol K). Here, in keeping with an odd tradition, mole is abbreviated as mol.

It turns out that only simple pure gases behave in the fashion as reported for the famous experiments mentioned above. By simple, we mean gases composed of single atoms or relatively small molecules. Gases that obey the equation of state given by Eq. (11.8) are therefore referred to as *ideal gases*. Further, Eq. (11.8) is called the *ideal gas law*. A more strict definition for an ideal gas will be given in the next section. This is not to say that the ideal gas law is not useful. Many of the gases one deals with from day to day are well described by it. These include CO, CO₂, N₂, He, H₂ and even CH₄ (methane).

When applying the gas law to the study of a gas we are often interested in changes of state. For example, if we change the temperature from say T_1 to T_2 how does this affect the pressure P ? There are three important changes of state that one needs to be especially aware of. In all of the changes of state considered here the amount of gas in the cylinder will remain constant.

First, consider the constant temperature change of state. This process is referred to as an *isothermal* change of state. Suppose if during an isothermal change of state, the volume goes from some initial value V_1 to some final value V_2 , and likewise for the pressure, then Eq. (11.8) leads to

$$P_1V_1 = P_2V_2, \quad \text{Isothermal change of state.} \quad (11.9)$$

Now suppose the volume were held constant while changing the pressure or temperature from an initial to final value. This change of state is called an *isochoric change of state*.

Again, from Eq. (11.8) we conclude that for an isochoric change of state

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}, \quad \text{Isochoric change of state.} \quad (11.10)$$

Finally, we want also to consider the constant pressure change of state. This change of state is referred to as an *isobaric change of state*. From Eq. (11.8) we conclude that

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \quad \text{Isobaric change of state.} \quad (11.11)$$

Example 11.3

3.00 mol of an ideal gas undergoes an isothermal compression at 120.0 °C. The gas has an initial pressure of 2.0 atm. After the change of state the new pressure of the gas is 3.0 atm. What was the initial and final volume for the gas?

It is given, that the change of state was a compression, that is, the volume of the gas was reduced. This information was not necessary for our analysis as the result will show that a compression occurred.

First, use the ideal gas law to compute the initial volume V_1 :

$$V_1 = \frac{nRT}{P_1} = \frac{(3.00)(8.314)(393)}{2.0 \times 10^5} \simeq 0.049 \text{ m}^3,$$

where we have used the fact that 1.0 atm $\simeq 1.0 \times 10^5$ Pa and 0 °C $\simeq 273$ K to convert all to SI units.

Now Eq. (11.9) can be used to compute the final volume:

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(2.0 \times 10^5)(0.049)}{3.0 \times 10^5} \simeq 0.033 \text{ m}^3.$$

Since $V_2 - V_1 < 0$ there was a reduction in the volume of the gas and therefore a compression occurred.

Example 11.4

An ideal gas initially at 100.0 °C occupying a volume of 0.250 liter (L) has a pressure of 1.00 atm. The gas then undergoes an isobaric change of state to the new temperature of 150.0 °C. How many moles of gas are present and what is the final volume for the gas?

Here we see the volume given in liters (L). Though this is not the SI unit for volume it is a unit commonly used by scientists and engineers. Further, the pressure is given in atmospheres (atm), another commonly used unit. When you have these units for volume and pressure it is convenient to use the gas constant with units of L atm/(mol K) rather than have it in units of J/(mol K). It is in these units

$$R = 0.0820 \frac{\text{L atm}}{\text{mol K}}$$

We use the ideal gas law to get n

$$n = \frac{PV_1}{RT_1} = \frac{(1.00)(0.250) \text{ L atm}}{(0.082 \frac{\text{L atm}}{\text{mol K}})(373 \text{ K})} \simeq 8.17 \times 10^{-3} \text{ moles .}$$

Now, Eq. (11.11) can be used to compute the final volume

$$V_2 = \frac{T_2 V_1}{T_1} = \frac{(423 \text{ K})(0.250 \text{ L})}{373 \text{ K}} \simeq 0.280 \text{ L .}$$

11.4 The Kinetic Theory of Gases

It is reasonable to propose that what we sense as temperature in the macroscopic world is associated with the motion of atoms and molecules at the microscopic level. This is a convenient idea since we can use the tools developed in the study of mechanics to deal with these minute particles. For example, one could compute the total kinetic energy of a gas liquid or solid if some knowledge of the mass and speed of the individual particles were known. Then, possibly a connection could be found between this kinetic energy and the temperature of the sample. This connection is the objective of the *kinetic theory of gases*.

Suppose you have a solid container and let it be filled on Earth with air at 1.0 atm. Now, the container is sealed. A pressure gauge, that detects the pressure in its interior, reads 1.0 atm. The container of gas is now taken into vacuum far from the gravitational influence of Earth or any other large object. What would the gauge read? Of course it still reads 1.0 atm. Why is this? You might recall from a previous chapter we learned that the pressure P a depth h within a fluid of density ρ is given by ρgh . So how is it that there is a pressure here where $g \approx 0$? First, we recall that $P = \rho gh$ was mostly used for the study of pressure within liquids—it only crudely approximates the pressure at the bottom of an atmosphere. It turns out that the pressure of a gas, within a closed container, is related to the motion of the atoms or molecules inside, not gravity.

To develop the kinetic theory of gases several postulates must be stated that also serve to specifically describe an ideal gas.

1. For temperatures above 0 K the particles of the gas, (atoms or molecules), are in constant motion in random directions with a range of possible speeds.
2. The gas particles do not exert any field force on one another. (For example, a gravity force).
3. The gas particles are point-like. That is, they do not occupy any of the gas volume.
4. Collisions between particles or particles with container walls can be described as perfectly elastic collisions.

With these postulates in mind, we now seek to derive an expression for the pressure of an ideal gas in a sealed container in a way that does not involve gravity. Let us consider a sealed cubic container of side length l which contains N atoms of an ideal gas at some fixed temperature T . The atoms are in random motion at all times. Consider one atom that strikes the left side of the container as depicted in Fig. 11.4.

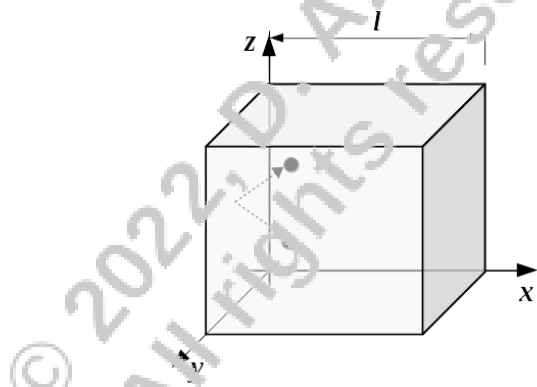


Figure 11.4: A cubic container of ideal gas. One of the gas atoms is depicted striking then, bouncing off the left side.

We would like to use our ideas from the study of Newton's laws of motion to derive an expression involving a quantity of interest in thermal physics like say the pressure. Therefore, we seek a description of the force involved when an atom strikes the wall of the container. When an atom strikes the left face, as shown in Fig. 11.4, there is a change in momentum Δp given by

$$\Delta p = mv_x - (-mv_x) = 2mv_x . \quad (11.12)$$

Here only the x component of the velocity is considered since there is no change in the momentum in the y and z direction in this case. We know from the chapter on Newton's laws of motion that the magnitude of a force F can be written as a change in momentum magnitude divided by time. Here, we propose to use the time interval between such collisions. This can be approximated as the time, t , required for the atom to travel from one side to

the other and back again or simply, $t = 2l/v_x$. Therefore we get for the force involved in this collision

$$F = \frac{mv_x^2}{l}. \quad (11.13)$$

Since there are N atoms in the container the total force on the container due to all such collisions would be

$$F = \frac{m}{l} \sum_{i=1}^N v_{xi}^2. \quad (11.14)$$

Since the speed of the atoms might vary, from one to the other, it would be more convenient to write the above in terms of the mean of the square of the speeds $\overline{v_x^2}$. This is simply

$$\overline{v_x^2} = \frac{\sum_{i=1}^N v_{xi}^2}{N}. \quad (11.15)$$

On comparing Eqs. (11.15) and (11.14) we find that the total magnitude of the force becomes

$$F = \frac{m}{l} N \overline{v_x^2}. \quad (11.16)$$

Now, it would be even better to have the above result written in terms of the mean of the square of the velocity magnitude, v , for atoms in the box, not a velocity component like v_x . From our study of vectors, it is known that $v^2 = v_x^2 + v_y^2 + v_z^2$. Since the particle motion is random it must be that $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$, so that

$$\overline{v^2} = 3\overline{v_x^2}. \quad (11.17)$$

Using Eq. (11.17) in Eq. (11.16) and dividing by the area of the side l^2 and then letting the volume l^3 be given by V we arrive at our expression for the pressure due to collision of particles with the walls of the container.

$$P = \frac{mN\overline{v^2}}{3V}. \quad (11.18)$$

If our model here is a good one, it ought to agree in some sense with the empirical result discussed in the previous section, that is Eq. (11.8). Eq. (11.8) is written in terms of moles and Eq. (11.18) is given in terms of the number of particles. So to compare these expressions let us rewrite our ideal gas law in terms of N .

The number of particles in a mole is a quantity referred to as Avogadro's number N_A . So it must be that the moles of gas n can be given by $n = N/N_A$. We define a new constant, *Boltzmann's constant* k as:

$$k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J/K}. \quad (11.19)$$

Here, R is the gas constant from the previous section and this new assignment for the symbol k , should not be confused with the wave number or spring constant from previous chapters. Using the fact that $n = N/N_A$, and Eq. (11.19), the ideal gas law of Eq. (11.8) can also be given in terms of Boltzmann's constant.

$$PV = NkT. \quad (11.20)$$

Now, we can equate Eq. (11.18) with the ideal gas law as given by Eq. (11.20). After reorganizing Eq. (11.18) a bit, we have for both results to agree that

$$\frac{2}{3}N \left(\frac{1}{2}m\overline{v^2} \right) = NkT . \quad (11.21)$$

From our study of energy we recognize that the factor in parenthesis on the left side of Eq. (11.21) is just the average kinetic energy for a particle in the ideal gas. So, we have agreement between the model involving kinetic theory and the empirical model when

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT . \quad (11.22)$$

This result is indeed reasonable and very useful in that it relates the mechanical properties of the gas with the thermal. When a particle translates in three dimensions, as is the case here, we say that the particle has three *degrees of freedom*. Therefore, we make the claim that each degree of freedom contributes $kT/2$ towards the total kinetic energy of the gas.

From this we conclude that, in an ideal gas, temperature is directly proportional to the average kinetic energy of the particles in the gas. Though this result is, strictly speaking, only applicable to the ideal gas, the student should memorize that in general what we sense as temperature in the macroscopic world can be related to the motion of particles at the atomic and molecular level.

Example 11.5

Hydrogen gas (H_2) is held in a sealed container at 400.0 K. What is the RMS speed for a particle in this gas?

Here you are asked for the *RMS* speed. RMS is an acronym for *square root of the mean of the squares*. This is an idea from statistics and it is a little like the algebraic mean of a set of data points in that it gives us an idea of what on average the values in the data set are like. RMS speeds are often used to describe atomic and molecular speeds. Let the RMS speed be given by v_{RMS} then

$$v_{RMS} = \sqrt{\overline{v^2}} .$$

This is quite convenient since we have the mean of the squares in Eq. (11.22). Solving Eq. (11.22) for $\overline{v^2}$ and taking the square root of both sides and simplifying yields

$$v_{RMS} = \sqrt{\frac{3kT}{m}} .$$

For H_2 we use the mass of two protons. Putting it all together gives

$$v_{RMS} = \sqrt{\frac{3(1.38 \times 10^{-23})(400.0)}{2(1.6726 \times 10^{-27})}} \simeq 2,227 \text{ m/s} .$$

11.5 Distribution of Speeds

In the previous section, the important results depended upon knowledge of the speed of the atoms in the container. With the number of atoms on the order of say 10^{23} it would be quite a task to track the speeds of each particle. A better approach is to assume that the speed of the particles are distributed in some random fashion about their mean value. If we could measure the speeds of individual particles we would find that some were slow and some were moving faster and eventually a mean of the distribution of values would likely develop. Statisticians have already developed certain mathematical functions that serve to describe such distributions. With such a function known, along with a mean speed, we can assign to each particle in the assembly a probability for having any speed other than the mean value.

In the 19th century, Scottish Physicist James Clerk Maxwell (1831-1879) proposed letting the number of particles in a gas having speed v be given by

$$f(v) = Cv^2 e^{-\frac{mv^2}{2kT}} \quad (11.23)$$

where C is a constant. To see how this equation describes the distribution of speeds in an assembly of gas particles, we consider a plot of f/C versus v for a non-realistic but instructive case. For the purposes of studying the shape of the distribution function we will keep things numerically convenient and let $m/(2kT) = 1$.

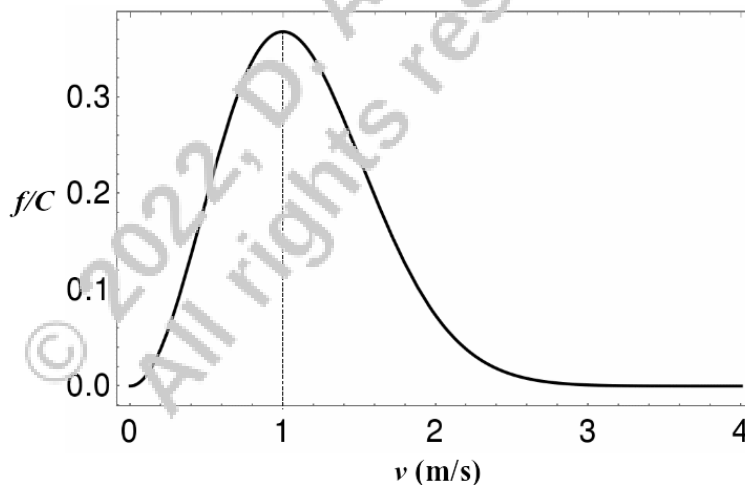


Figure 11.5: Maxwell distribution of speeds for $m/(2kT) = 1$. The most probable speed is where $f(v)$ is a maximum denoted here by the dashed line.

In Fig 11.5, the most probable speed is given by the vertical dashed line. Clearly, the distribution predicts that most particles will have a speed near the most probable value, some slightly faster some slower. However, speeds far from the most probable are unlikely. Extreme speeds, either very slow or super fast, are essentially forbidden.

Since $f(v)$ gives the number of particles having speed v it must be that

$$N = \int_0^{\infty} f(v) dv . \quad (11.24)$$

Example 11.6

Use Eq. (11.24) to determine a value for the constant C in Eq. (11.23).

We must have that

$$N = C \int_0^\infty v^2 e^{-\frac{mv^2}{2kT}} dv .$$

To simplify things we let $a = m/(2kT)$. The above becomes

$$N = C \int_0^\infty v^2 e^{-av^2} dv .$$

Functions of the type, e^{-av^2} , as appear in the integrand above, are referred to as a *Gaussian*. These functions have the convenient property that many definite integrals, in which they are involved, can be computed. For example, the integral above is readily found in most tables of integrals. Using a result from an Appendix we get

$$N = \frac{C}{4a} \sqrt{\frac{\pi}{a}} .$$

Solving for C and rearranging leads to

$$C = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2}$$

So we can write the Maxwell distribution of speeds as

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}} . \quad (11.25)$$

Example 11.7

Use Eq. (11.25) to compute the mean speed \bar{v} for the Maxwell distribution of speeds.

The sum of all particle speeds will be $\int_0^\infty v f(v) dv$, So, the mean speed is given by

$$\bar{v} = \frac{\int_0^\infty v f(v) dv}{N} .$$

Using Eq. (11.25) in this we get

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv .$$

The solution for this definite integral can be found in a table in an appendix. Its result leads to

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{2(kT)^2}{m^2} = \sqrt{\frac{8kT}{m\pi}} .$$

As you will learn in a problem at the end of this chapter, the mean speed for the Maxwell distribution is not equivalent to the most probable speed.

11.6 The van der Waals Equation of State

We will discuss briefly, in this section, a famous equation of state that was created in order to deal with gases that do not exhibit ideal gas behavior. This well-known equation of state was developed as an improvement to the ideal gas law. Two of the *idealizations* used to formulate the ideal gas law are replaced with more realistic assumptions. It is interesting to see how these changes are incorporated within the existing model to yield a new equation of state.

First, we all know that atoms and molecules are not really point like. That is, they take up some of the actual space in the container. So the presence of the particles should slightly reduce the volume available to the gas. Also, many gaseous particles exert a field force on one another. For example, it is reasonable to propose that when they encounter one another there is a mildly attractive field force between them. After all, when the temperature gets low enough the gaseous particles will condense into a liquid. This effect would decrease the rate at which particle-wall collisions occur and therefore slightly decrease the pressure. The van der Waals equation cleverly takes into account these two effects.

To see how this is done, let's consider the ideal gas law again here: $PV = nRT$. To achieve the adjustment to the gas volume due to the finite size of the particles we subtract from the gas volume a term which is directly proportional to the amount of gas in the container. This gives the following adjusted gas law

$$P(V - nb) = nRT . \quad (11.26)$$

Here b is a constant whose value depends upon the type of gas in the container. The new pressure is then

$$P = \frac{nRT}{(V - nb)} . \quad (11.27)$$

Now, we consider the attractive field force between particles. In the bulk of the gas one could expect that the force due to particles on the left would counteract that due to those on the right. However, for the layer of particles next to a surface there would be a net attractive force pulling them back into the center of the chamber (Assuming no attraction between the container wall and the particle). Since we are considering a force between layers of particles it will be assumed that this effect is directly proportional to the square of the density of particles in the gas. Since we are dealing with moles of gas we write this in terms of molar density and some constant as $a(n/V)^2$. Adjusting the pressure given by Eq. (11.27) by this amount we get

$$P = \frac{nRT}{(V - nb)} - a \left(\frac{n}{V} \right)^2 . \quad (11.28)$$

With a little rearranging one now arrives at the van der Waals equation of state

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] (V - nb) = nRT . \quad (11.29)$$

The constants a and b are referred to as van der Waals constants. Table 11.3 lists some of these constants for several common gases.

Table 11.3: van der Waals constants for various gases.

Substance	a (atm L ² /mol ²)	b (L/mol)
Argon	1.337	0.0320
Butane	13.70	0.1164
Ethane	5.506	0.0651
Fluorine	1.156	0.0290
HBr	4.441	0.0442

Example 11.8

A 2.00 L container has within it 0.0100 moles of Ethane gas at 200.0 °C. Compute the pressure for this gas using the ideal gas law and the van der Waals equation of state. Comment on the difference between the two results.

Solve Eq. (11.8) for pressure P :

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

Since volume is given in liters we will use the L atm/(mol K) version of the gas constant.

$$P = \frac{0.0100 \text{ mol} (0.082 \frac{\text{L atm}}{\text{mol K}}) (473 \text{ K})}{2.00 \text{ L}} \simeq 0.1939 \text{ atm} .$$

To compute the van der Waals version of the pressure we use Eq. (11.28). We get the van der Waals constants from Table 11.3

$$P = \frac{0.0100 \text{ mol} (0.082 \frac{\text{L atm}}{\text{mol K}}) (473 \text{ K})}{2.00 \text{ L} - (0.0100 \text{ mol}) (0.0651 \text{ L/mol})} - (5.506 \text{ atm L}^2/\text{mol}^2) \left(\frac{0.0100 \text{ mol}}{2.00 \text{ L}} \right)^2 = 0.1938 \text{ .}$$

From these results, it can be seen that the two equations of state yield similar results. Only at higher gas densities does a significant differences between the two pressures begin to appear. Therefore, the ideal gas law very effectively describes low density gases otherwise known as *rarefied* gases.

11.7 Gaseous Diffusion

As a final topic for this chapter, we will discuss the notion of gaseous diffusion. Suppose you have a sealed container with some pure gas, say argon, at 1.0 atm of pressure. You then open this container and release the gas into the surrounding air which is also at 1.0 atm. Even though the pressures are equivalent, the argon atoms will spontaneously move into the region around the once sealed container, mixing with the atoms and molecules that make up

the air. This is a process known as diffusion. It would be useful to know the rate at which the argon atoms are moving out of the container. A relation known as *Fick's first law* is useful for quantifying this effect.

To deal with this famous law we first have to become familiar with the idea of particle flux. Suppose the opening of the container is rectangular in shape with area A . Then the number of argon particles crossing this area per unit time is called the flux, J . Therefore, it is a measure of particle flow. The SI unit for J would be $\text{m}^{-2}\text{s}^{-1}$. Another quantity we need to define here would be the concentration, c , of argon atoms. This would give the number of argon atoms per unit volume of space. The SI unit for concentration would be m^{-3} . A cartoon depiction of this process is shown below in Fig. 11.6.

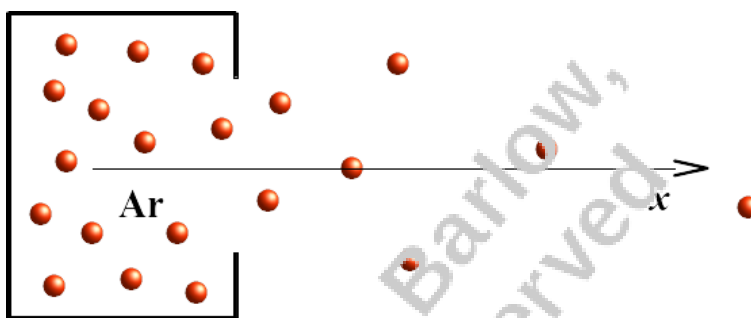


Figure 11.6: Argon atoms diffusing from a container into the surrounding air.

For simplicity, we will assume that the process can be studied in one dimension. That is, we will be interested in the flux and the concentration only along the x axis shown in Fig. 11.6. Fick's first law states that the flux of argon atoms, as a function of position, $J(x)$, is directly proportional to the first derivative of the concentration with respect to position at that point. In other words, $J \propto dc/dx$. So, introducing a constant of proportionality, one can write Fick's first law as

$$J = -D \frac{dc}{dx}. \quad (11.30)$$

Here D is called the *diffusion coefficient* or simply the *diffusivity*. Its value depends upon the particular species undergoing diffusion and the surrounding medium. The negative sign in Eq. (11.30) is there because we want a concentration that is decreasing with increasing x , that is, a negative derivative, to yield a flux that is flowing in the positive direction which is what would be observed. Diffusion coefficients for various substances in air are listed in Table 11.4.

Fick's first law has been discussed here for the case of gaseous diffusion but it is also a useful principle when studying the diffusion of a species within a liquid.

Table 11.4: Diffusion coefficients for various gases in air at 1.0 atm and 20 °C.

Substance	D (1.0×10^{-4} m ² /s)
Ar	0.189
CO	0.208
Methane	0.210
He	0.697
H ₂	0.756

Example 11.9

Helium gas has been released from a container into air. It is known, that at some instant in time, the concentration of He as a function of distance, $c(x)$, from the container, can be given by

$$c(x) = c_o e^{-kx} .$$

Where $c_o = 0.179$ kg/m³ and $k = 0.20$ m⁻¹. Find an expression for the flux of He in air, at this point in time, as a function of position $J(x)$. What is the flux at 0.5 m from the source and at 10.0 m from the source at this instant in time?

To get $J(x)$ we simply use Fick's first law:

$$J = -D \frac{d}{dx} c_o e^{-kx} = Dk c_o e^{-kx} .$$

Now, we evaluate this result at the two distances. Using the value for D from Table 11.4 we get

0.5 m:

$$J(0.5) = (0.697 \times 10^4)(0.2)(0.179)e^{-(0.2)(0.5)} \simeq 226 \text{ m}^{-2}\text{s}^{-1} .$$

10.0 m:

$$J(10) = (0.697 \times 10^4)(0.2)(0.179)e^{-(0.2)(10.0)} \simeq 33.8 \text{ m}^{-2}\text{s}^{-1} .$$

These results give us more information than knowing the concentration alone. Knowledge of the flux gives us a rate of flow. Here we see that more helium is flowing away from the container, per unit time, at 0.5 m than at 10.0 m. It should be noted that in this problem flux was computed for just one instant in time since in reality, c and thus J could vary with time.

11.8 PROBLEMS

11.1 Use the result from Example 11.1 to derive an expression to convert from degrees Celsius to degrees Fahrenheit.

11.2 Astronomers tell us that the core of the Sun is at a temperature of 1.5×10^7 K. Convert this value to degrees Celsius and Fahrenheit.

11.3 At what temperature do the Celsius and Fahrenheit scales give the same value?

11.4 An aluminum power line is 5.0 km in length when installed at 25.0°C . By how much does its length increase on a day when the temperature is 38.0°C ?

11.5 An unknown material, in the shape of a thin rod, has length l_o at 25.0°C . It is found that $\Delta l/l_o = 1.0 \times 10^{-5}$ for any $\Delta T = 5.0$ K. What is its coefficient of linear expansion? Judging from the quantities in Table 11.1 do you think the material is a metal or ceramic material?

11.6 A gold ring has a diameter of 1.5 cm at 25.0°C . If it is heated up to 40.0°C what is the new diameter?

11.7 A flat metal plate undergoes thermal expansion and has a change in length Δl and change in width Δw as shown in the figure below.

Let the initial area of the plate be A_o . Use the idea of linear expansion to show that the change in area, ΔA , of the plate due to temperature increase ΔT can be given by

$$\Delta A = 2\alpha w_o l_o \Delta T + \alpha^2 A_o \Delta T^2 .$$

A good approximation is to let

$$\Delta A \approx 2\alpha w_o l_o \Delta T .$$

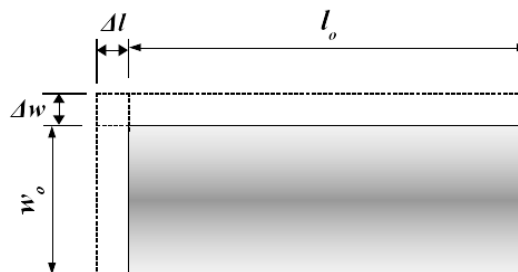


Figure 11.7: A flat metal plate expands due to the increase in temperature ΔT .

Why is this?

11.8 On a hot day, a gasoline truck pumps gas from the truck into an underground tank that is initially empty. The gas in the truck is initially at 100.0°F . The meter on the truck records the transmission of 1,000 gallons of gas from the truck into the tank. The underground tank is at the temperature of 72.0°F . After the gas cools to this temperature the service station manager notices that he does not have 1,000 gallons in his tank. By how much does he appear to be short? (Use the volume expansion coefficient for octane).

11.9 0.030 moles of helium gas initially at 1.00×10^5 Pa and 300.0 K undergo an isochoric change of state to the new pressure of 1.40×10^5 Pa. What is the final temperature of the gas?

11.10 0.010 m^3 of ideal gas is held in a container at a pressure of 1.50×10^5 Pa. This gas undergoes an isothermal expansion to a new volume of 0.0200 m^3 . What is the pressure after the expansion?

11.11 Consider three isothermal expansions for an ideal gas at the temperatures T_1 , T_2 and T_3 where $T_3 > T_2 > T_1$. For each case sketch the curve given by pressure vs. volume. Curves of this sort are referred to as *isotherms* on the *PV* plane.

11.12 0.020 moles of ideal gas undergo an isochoric change of state where the pressure is doubled. If its initial temperature was T what is the final temperature of the gas.

11.13 An ideal gas, initially at temperature T , undergoes an isobaric expansion which doubles its volume. It then undergoes an isochoric change where its pressure is halved.

What is the temperature of the gas after both changes?

11.14 Show that for the Maxwell distribution of speeds, Eq. (11.25), the most probable speed, v_{mp} is given by

$$v_{mp} = \sqrt{\frac{2kT}{m}}.$$

11.15 Consider a sample of 0.5 moles of helium gas at 330 K. The number of atoms, ΔN , having speeds within the range Δv can be estimated as $\Delta N = f(v)\Delta v$, where $f(v)$ is the Maxwell distribution of speeds. How many helium atoms in this sample have speeds between 100 m/s and 110 m/s? (The mass of the helium atom is $m = 6.65 \times 10^{-27}$ kg)

11.16 For any dynamical quantity $q(v)$, (some quantity that is a function of particle speed), the mean value of the quantity \bar{q} for the Maxwell distribution is given by

$$\bar{q} = \frac{\int_0^\infty qf(v)dv}{N}.$$

Use this fact to determine the mean kinetic energy of the Maxwell distribution.

11.17 Unlike the ideal gas law, the van der Waals equation of state predicts the occurrence of critical points, a phenomena observed for real gases. A critical point occurs when

$$\frac{\partial P}{\partial V} = 0 \text{ and } \frac{\partial^2 P}{\partial V^2} = 0.$$

At this point the pressure, temperature and volume have the so called critical values P_c , V_c , and T_c . Show that

$$T_c = \frac{2an}{RV_c^3}(V_c - nb)^2,$$

for the van der Waals gas.

11.18 The concentration c for Methane (CH_4) in air in a region is given by

$$c(x) = (0.0233 \text{ kg/m}^4)x.$$

Determine the flux for methane in this region. Is this flux a function of position? Does CH_4 flow to the left or right.

11.19 The flux for a gas diffusing in space is given by

$$J(x) = j_0 e^{-kx},$$

where j_0 and k are constants. Find the concentration $c(x)$. Assume that $c(0) = c_0$ and $c \rightarrow 0$ as $x \rightarrow \infty$.

11.20 The diffusion coefficient for most gases varies with temperature T . This can be estimated by

$$D(T) = D_0 e^{-E_a/kT}.$$

Here D_0 is a constant and E_a an activation energy. Suppose that $E_a \approx 0.2 \times 10^{-19}$ J, Determine D_0 for all of the gases listed in Table 11.4.

11.21 A thin copper rod has length l_0 at room temperature. The temperature of the rod is then increased by 40.0 K. For an aluminum rod to have the same length expansion over the same temperature range what must its initial length be?

11.22 A metal bridge covers a span of 0.25 miles. It has two expansion joints both 3.0 cm in width when the temperature is 25.0 °C. The temperature increases one day to 40.0 °C. Are the expansion joints wide enough? (Estimate this by modeling the bridge as a thin iron rod).