

Essay 1: Pressure and Forces

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Pressure and Forces

In the mining industry, the roof (hangingwall) tends to drop as the face of the tunnel (stope) is excavated for rock containing gold.

As one can imagine, a roof falling on one's head is not a nice prospect! Therefore the roof needs to be supported.

The roof is not one big uniform chunk of rock. Rather it is broken up into smaller chunks. It is assumed that the biggest chunk of rock in the roof has a mass of less than 20 000 kgs therefore each support has to be designed to resist a force related to that mass. The strength of the material (either wood or steel) making up the support is taken into account when working out the minimum required size and thickness of the parts to withstand the force of the roof.

Sometimes the design of the support is such that the support needs to withstand the rock mass without the force breaking the roof..

Therefore hydraulic supports (hydro = water) use the principles of force and pressure such that as a force is exerted on the support, the water pressure increases. A pressure relief valve then squirts out water when the pressure (and thus the force) gets too large. Imagine a very large, modified doctor's syringe.

In the petrochemical industry, there are many vessels and pipes that are under high pressures. A vessel is a containment unit (Imagine a pot without handles, that has the lid welded to the pot that would be a small vessel) where chemicals mix and react to form other chemicals, amongst other uses.

The end product chemicals are sold to companies that use these chemicals to make shampoo, dishwashing liquid, plastic containers, fertilizer, etc. Anyway, some of these chemical reactions require high temperatures and pressures in order to work. These pressures result in forces being applied to the insides of the vessels and pipes. Therefore the minimum thickness of the pipe and vessels walls must be determined using calculations, to withstand these forces. These calculations take into account the strength of the material (typically steel, plastic or composite), the diameter and of course the pressure inside the equipment. Let examine the concepts of force and pressure in further detail.

Chapter 1

Heat and Properties of Matter

1.1 Phases of matter

1.1.1 Density

Matter is a substance which has mass and occupies space. The density of matter refers to how much mass is in a given volume. Said differently, you can imagine the density to be the amount of mass packed into a given volume.

$$\text{density} = \frac{\text{Mass}}{\text{Volume}}$$

If we consider a bar of soap and a bar of steel with the same volume, the steel will have more mass because it has a greater density. The density is greater in steel because more atoms are closely packed in comparison to the soap. Although they are both the same size, the bar of steel will be "heavier" because it has more mass.

Worked Example 1

Density of objects

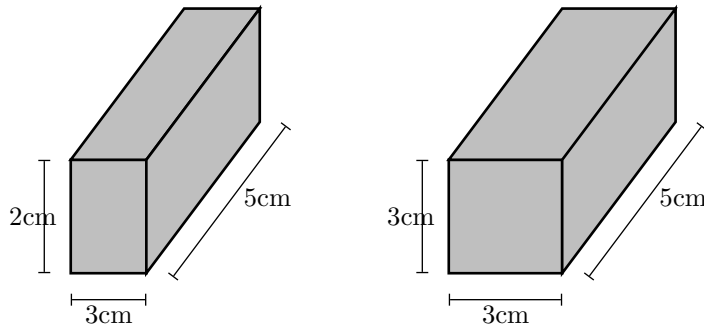
A bar of aluminum (Al) has dimensions 2cm x 3cm x 5cm with a mass of 81g. A bar of lead (Pb) has dimensions 3cm x 3cm x 5cm and a mass of 510.3g. Calculate the density of the aluminum and lead.

Solution:

First we calculate the volume of Al and Pb:

$$\text{volume} = \text{Length} * \text{Width} * \text{Height}$$

For Aluminum: $\text{volume} = 2\text{cm} * 3\text{cm} * 5\text{cm} = 30\text{cm}^3$



For Lead: $volume = 3cm * 3cm * 5cm = 45cm^3$

We can now calculate the densities using the mass and volume of each material.

$$\text{For Aluminum: } density = \frac{81g}{30cm^3} = 2.7g/cm^3$$

$$\text{For Lead: } density = \frac{510.3g}{45cm^3} = 11.34g/cm^3$$

Now that you know the density of aluminum and lead, which object would be bigger (larger volume): 1kg of Lead or 1kg of Aluminum.

Solution:

1kg of aluminum will be much larger in volume than 1kg of lead. Aluminum has a smaller density so it will take a lot more of it to have a weight of 1kg. Lead is much more dense, so it will take less for it to weigh 1kg.

The density of liquids and gases can be calculated the same way as in solids. If the mass and volume of a liquid is known, the density can be calculated. We can often determine which liquid has a greater density by mixing two liquids and seeing how they settle. The more dense liquid will fall towards the bottom, or 'sink'. If you have ever added olive oil to water, you have seen it sits on the surface, or 'floats'. This is because olive oil is less dense than water. Fog occurs when water vapor becomes more dense than air ("a cloud that sinks in air").

This principle can be used with solids and liquids. In fact, it is the density of an object that determines if it will float or sink in water. Objects with densities greater than water will sink.

Worked Example 2

Objects floating in water

Ivory soap is famous for "soap that floats". If a 5cm x 3cm x 10cm bar of ivory soap weighs 1.35 Newtons, show that its density is less

than water.

Solution:

First calculate the bars volume: $volume = 3cm * 5cm * 10cm = 150cm^3$

Now we must determine the mass of the bar based on its weight. We will use Newton's Second law ($F = ma$):

$$Weight = mass * gravity \implies Weight = 9.8m/s^2 * Mass$$

$$Mass = \frac{1.35N}{9.8m/s^2} = .138kg$$

Using the mass and the volume we determine the density of the soap:

$$density = \frac{138g}{150cm^3} = .92g/cm^3$$

Water has a density of $1g/cm^3$, therefore the soap is less dense than water, allowing it to float.

1.2 Phases of matter

Although phases are conceptually simple, they are hard to define precisely. A good definition of a phase of a system is a region in the parameter space of the system's thermodynamic variables in which the free energy is analytic. Equivalently, two states of a system are in the same phase if they can be transformed into each other without abrupt changes in any of their thermodynamic properties.

All the thermodynamic properties of a system – the entropy, heat capacity, magnetization, compressibility, and so forth – may be expressed in terms of the free energy and its derivatives. For example, the entropy is simply the first derivative of the free energy with temperature. As long as the free energy remains analytic, all the thermodynamic properties will be well-behaved.

When a system goes from one phase to another, there will generally be a stage where the free energy is non-analytic. This is known as a phase transition. Familiar examples of phase transitions are melting (solid to liquid), freezing (liquid to solid), boiling (liquid to gas), and condensation (gas to liquid). Due to this non-analyticity, the free energies on either side of the transition are two different functions, so one or more thermodynamic properties will behave very differently after the transition. The property most commonly examined in this context is the heat capacity. During a transition, the heat capacity may become infinite, jump abruptly to a different value, or exhibit a "kink" or discontinuity in its derivative.

In practice, each type of phase is distinguished by a handful of relevant thermodynamic properties. For example, the distinguishing feature of a solid is its rigidity; unlike a liquid or a gas, a solid does not easily change its shape. Liquids are distinct from gases because they have much lower compressibility:

a gas in a large container fills the container, whereas a liquid forms a puddle in the bottom. Many of the properties of solids, liquids, and gases are not distinct; for instance, it is not useful to compare their magnetic properties. On the other hand, the ferromagnetic phase of a magnetic material is distinguished from the paramagnetic phase by the presence of bulk magnetization without an applied magnetic field.

To take another example, many substances can exist in a variety of solid phases each corresponding to a unique crystal structure. These varying crystal phases of the same substance are called polymorphs. Diamond and graphite are examples of polymorphs of carbon. Graphite is composed of layers of hexagonally arranged carbon atoms, in which each carbon atom is strongly bound to three neighboring atoms in the same layer and is weakly bound to atoms in the neighboring layers. By contrast in diamond each carbon atom is strongly bound to four neighboring carbon atoms in a cubic array. The unique crystal structures of graphite and diamond are responsible for the vastly different properties of these two materials.

Metastable phases

Metastable states may sometimes be considered as phases, although strictly speaking they aren't because they are unstable. For example, each polymorph of a given substance is usually only stable over a specific range of conditions. For example, diamond is only stable at extremely high pressures. Graphite is the stable form of carbon at normal atmospheric pressures. Although diamond is not stable at atmospheric pressures and should transform to graphite, we know that diamonds exist at these pressures. This is because at normal temperatures the transformation from diamond to graphite is extremely slow. If we were to heat the diamond, the rate of transformation would increase and the diamond would become graphite. However, at normal temperatures the diamond can persist for a very long time.

Another important example of metastable polymorphs occurs in the processing of steel. Steels are often subjected to a variety of thermal treatments designed to produce various combinations of stable and metastable iron phases. In this way the steel properties, such as hardness and strength can be adjusted by controlling the relative amounts and crystal sizes of the various phases that form.

Phase diagrams

The different phases of a system may be represented using a phase diagram. The axes of the diagrams are the relevant thermodynamic variables. For simple mechanical systems, we generally use the pressure and temperature. The following figure shows a phase diagram for a typical material exhibiting solid, liquid and gaseous phases.

The markings on the phase diagram show the points where the free energy is non-analytic. The open spaces, where the free energy is analytic, correspond to the phases. The phases are separated by lines of non-analyticity, where phase transitions occur, which are called phase boundaries.

In the above diagram, the phase boundary between liquid and gas does not continue indefinitely. Instead, it terminates at a point on the phase diagram called the critical point. This reflects the fact that, at extremely high temperatures and pressures, the liquid and gaseous phases become indistinguishable. In water, the critical point occurs at around 647 K (374 C or 705 F) and 22.064 MPa.

The existence of the liquid-gas critical point reveals a slight ambiguity in our above definitions. When going from the liquid to the gaseous phase, one usually crosses the phase boundary, but it is possible to choose a path that never crosses the boundary by going to the right of the critical point. Thus, phases can sometimes blend continuously into each other. We should note, however, that this does not always happen. For example, it is impossible for the solid-liquid phase boundary to end in a critical point in the same way as the liquid-gas boundary, because the solid and liquid phases have different symmetry.

An interesting thing to note is that the solid-liquid phase boundary in the phase diagram of most substances, such as the one shown above, has a positive slope. This is due to the solid phase having a higher density than the liquid, so that increasing the pressure increases the melting temperature. However, in the phase diagram for water the solid-liquid phase boundary has a negative slope. This reflects the fact that ice has a lower density than water, which is an unusual property for a material.

1.2.1 Solids, liquids, gasses

1.2.2 Pressure in fluids

1.2.3 change of phase

1.3 Deformation of solids

1.3.1 strain, stress

Stress (σ) and strain (ϵ) is one of the most fundamental concepts used in the mechanics of materials. The concept can be easily illustrated by considering a solid, straight bar with a constant cross section throughout its length where a force is distributed evenly at the ends of the bar. This force puts a stress upon the bar. Like pressure, the stress is the force per unit area. In this case the area is the cross sectional area of the bar.

$$\text{stress} = \frac{\text{Force}}{\text{Area}_{\text{crosssection}}} \implies \sigma = \frac{F}{A}$$

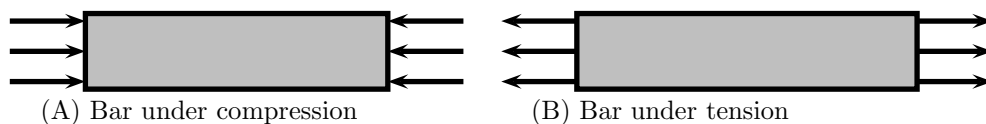


Figure 1.1: Illustration of Bar

The bar in figure 1a is said to be under compression. If the direction of the force (\vec{F}), were reversed, stretching the bar, it would be under tension (fig. 1b). Using intuition, you can imagine how the bar might change in shape under compression and tension. Under a compressive load, the bar will shorten and thicken. In contrast, a tensile load will lengthen the bar and make it thinner.



Figure 1.2: Bar changes length under tensile stress

For a bar with an original length L , the addition of a stress will result in change of length ΔL . With ΔL and L we can now define strain as the ratio between the two. That is, strain is defined as the fractional change in length of the bar:

$$Strain \equiv \frac{\Delta L}{L}$$

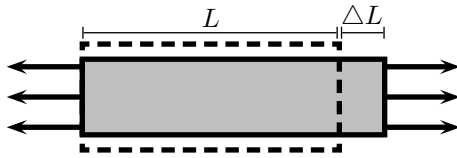


Figure 1.3: Left end of bar is fixed as length changes

1.3.2 Elastic and plastic behavior

Material properties are often characterized by a stress versus strain graph (figure x.xx). One way in which these graphs can be determined is by tensile testing. In this process, a machine stretches a the material by constant amounts and the corresponding stress is measured and plotted. Typical solid metal bars will show a result like that of figure x.xx. This is called a Type II response. Other materials may exhibit different responses. We will only concern ourself with Type II materials.

The linear region of the graph is called the elastic region. By obtaining the slope of the linear region, it is easy to find the strain for a given stress, or vice-

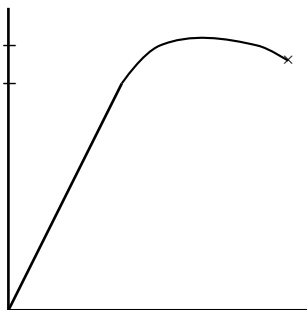


Figure 1.4: dashed line represents plastic recovery ****incomplete****

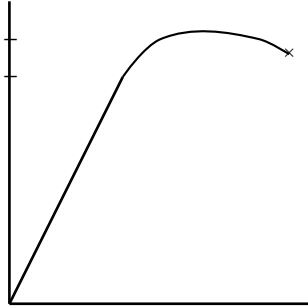


Figure 1.5: dashed line represents plastic recovery ****incomplete****

versa. This slope shows itself to be very useful in characterizing materials, so it is called the Modulus of Elasticity, or Young's Modulus:

$$E = \frac{\text{stress}}{\text{strain}} = \frac{F/A}{\Delta L/L}$$

The elastic region has the unique property that allows the material to return to its original shape when the stress is removed. As the stress is removed it will follow line back to zero. One may think of stretching a spring and then letting it return to its original length. When a stress is applied in the linear region, the material is said to undergo elastic deformation.

When a stress is applied that is in the non-linear region, the material will no longer return to its original shape. This is referred to as plastic deformation. If you have overstretched a spring you have seen that it no longer returns to its initial length; it has been plastically deformed. The stress where plastic behavior begins is called the yield strength (point A, fig x).

When a material has plastically deformed it will still recover some of its shape (like an overstretched spring). When a stress in the non-linear region is removed, the stress strain graph will follow a line with a slope equal to the modulus of elasticity (see the dashed line in figure x.xx). The plastically deformed material will now have a linear region that follows the dashed line.

Greater stresses in the plastic region will eventually lead to fracture (the material breaks). The maximum stress the material can undergo before fracture is the ultimate strength.

1.4 Ideal gasses

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Gérald Wigger started his Physics studies at ETH in Zuerich, Switzerland. He moved to Cape Town, South Africa, for his Bachelor of Science degree (with honours) in Physics from the University of Cape Town in 1998. Returned to Switzerland, he finished his Diploma at ETH in 2000 and followed up with a PhD in the Solid

State Physics group of Prof. Hans-Ruedi Ott at ETH. He graduated in the year 2004. Being awarded a Swiss fellowship, he moved to Stanford University where he is currently continuing his Physics research in the field of Materials with novel electronic properties.

Any liquid or solid material, heated up above its melting point, undergoes a transition into a gaseous state. For some materials such as iron, one has to heat up to several thousand degrees Celsius ($^{\circ}\text{C}$), whereas Helium is a gas already at -269°C . As we find very strong bonding between the atoms in a solid material, a gas consists of molecules which do interact very poorly. If one forgets about any electrostatic or intermolecular attractive forces between the molecules, one can assume that all collisions are perfectly elastic. One can visualize the gas as a collection of perfectly hard spheres which collide but which otherwise do not interact with each other. In such a gas, all the internal energy is in the form of kinetic energy and any change in internal energy is accompanied by a change in temperature. Such a gas is called an **ideal gas**.

In order for a gas to be described as an ideal gas, the temperature should be raised far enough above the melting point. A few examples of ideal gases at room temperature are Helium, Argon and hydrogen. Despite the fact that there are only a few gases which can be accurately described as an ideal gas, the underlying theory is widely used in Physics because of its beauty and simplicity.

A thermodynamic system may have a certain substance or material whose quantity can be expressed in mass or mols in an overall volume. These are extensive properties of the system. If the substance is evenly distributed throughout the volume in question, then a value of volume per amount of substance may be used as an intensive property. For an example, for an amount called a mol, volume per mol is typically called molar volume. Also, a volume per mass for a specific substance may be called specific volume. In the case of an ideal gas, a simple equation of state relates the three intensive properties, temperature, pressure, and molar or specific volume. Hence, for a closed system containing an ideal gas, the state can be specified by giving the values of any two of pressure, temperature, and molar volume.

1.4.1 Equation of state

1661 - Robert Boyle used a U-tube and Mercury to develop a mathematical relationship between pressure and volume. To a good approximation, the pressure and volume of a fixed amount of gas at a constant temperature were related by

$$p \cdot V = \text{constant} \quad (1.1)$$

In other words, if we compress a given quantity of gas, the pressure will increase. And if we put it under pressure, the volume of the gas will decrease proportionally.

Worked Example 3

compressed Helium gas

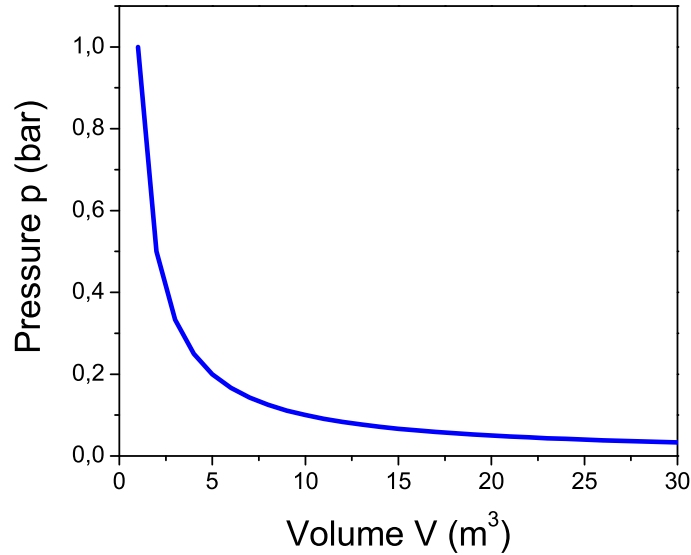


Figure 1.6: Pressure-Volume diagram for the ideal gas at constant temperature.

A sample of Helium gas at 25°C is compressed from 200 cm^3 to 0.240 cm^3 . Its pressure is now 3.00 cm Hg . What was the original pressure of the Helium?

Solution:

It's always a good idea to write down the values of all known variables, indicating whether the values are for initial or final states. Boyle's Law problems are essentially special cases of the Ideal Gas Law:

Initial: $p_1 = ?$; $V_1 = 200\text{ cm}^3$;

Final: $p_2 = 3.00\text{ cm Hg}$; $V_2 = 0.240\text{ cm}^3$;

Since the number of molecules stays constant and the temperature is not changed along the process, so

$$p_1 \cdot V_1 = p_2 \cdot V_2$$

hence

$$p_1 = p_2 \cdot V_2 / V_1 = 3.00\text{ cmHg} \cdot 0.240\text{ cm}^3 / 200\text{ cm}^3$$

Setting in the values yields $p_1 = 3.60 \cdot 10^{-3}\text{ cm Hg}$.

Did you notice that the units for the pressure are in cm Hg ? You may wish to convert this to a more common unit, such as millimeters of mercury, atmospheres, or pascals.

$$3.60 \cdot 10^{-3}\text{ Hg} \cdot 10\text{mm}/1\text{ cm} = 3.60 \cdot 10^{-2}\text{ mm Hg}$$

$$3.60 \cdot 10^{-3}\text{ Hg} \cdot 1\text{ atm}/76.0\text{ cm Hg} = 4.74 \cdot 10^{-5}\text{ atm}$$

One way to experience this is to dive under water. There is air in your middle ear, which is normally at one atmosphere of pressure to balance the air outside your ear drum. The water will put pressure on the ear drum, thereby compressing the air in your middle ear. Divers must push air into the ear through their Eustacean tubes to equalize this pressure.

Worked Example 4

pressure in the ear of a diver

How deep would you have to dive before the air in your middle ear would be compressed to 75% of its initial volume? Assume for the beginning that the temperature of the sea is constant as you dive.

Solution:

First we write down the pressure as a function of height h :

$$p = p_0 + \rho \cdot g \cdot h$$

where we take for p_0 the atmospheric pressure at height $h = 0$, ρ is the density of water at 20 degrees Celsius 998.23 kg/m^3 , $g = 9.81 \text{ ms}^{-2}$.

As the temperature is constant, it holds for both heights h

$$p_0 \cdot V_0 = (p_0 + \rho gh) \cdot V_e$$

Now solving for h using the fact that

$$V_e/V_0 = 0.75$$

yields

$$h = (0.75 * p_0 - p_0)/(\rho g)$$

Now, how far can the diver dive down before the membranes of his ear brake.

Solution:

As the result is negative, h determines the way he can dive down. h is given as roughly 2.6 m.

In 1809, the French chemist Joseph-Louis Gay-Lussac investigated the relationship between the Pressure of a gas and its temperature. Keeping a constant volume, the pressure of a gas sample is directly proportional to the temperature. Attention, the temperature is measured in Kelvin! The mathematical statement is as follows:

$$p_1/T_1 = p_2/T_2 = \text{constant}$$

That means, that pressure divided by temperature is a constant. On the other hand, if we plot pressure versus temperature, the graph crosses 0 pressure for $T = 0 \text{ K} = -273.15 \text{ }^\circ\text{C}$ as shown in the following figure. That point is called the **absolute Zero**. That is where any motion of molecules, electrons or other particles stops.

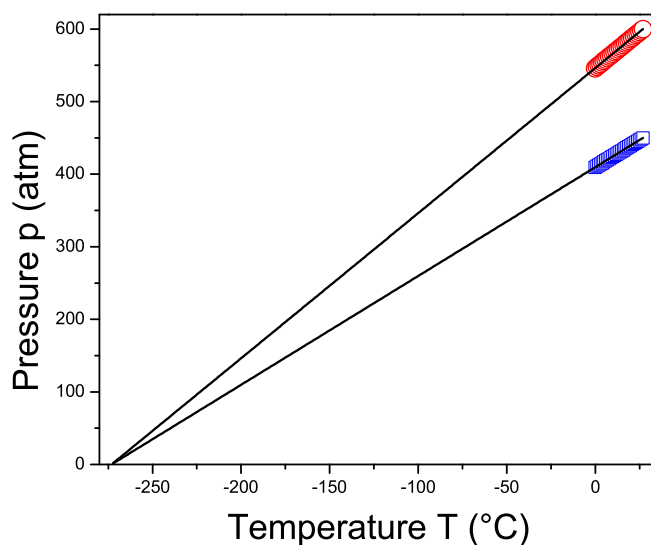


Figure 1.7: Pressure-temperature diagram for the ideal gas at constant volume.

Worked Example 5

Gay-Lussac

Suppose we have the following problem:

A gas cylinder containing explosive hydrogen gas has a pressure of 50 atm at a temperature of 300 K. The cylinder can withstand a pressure of 500 atm before it bursts, causing a building-flattening explosion. What is the maximum temperature the cylinder can withstand before bursting?

Solution: Let's rewrite this, identifying the variables:

A gas cylinder containing explosive hydrogen gas has a pressure of 50 atm (p_1) at a temperature of 300 K (T_1). The cylinder can withstand a pressure of 500 atm (p_2) before it bursts, causing a

building-flattening explosion. What is the maximum temperature the cylinder can withstand before bursting?

Plugging in the known variables into the expression for the Gay-Lussac law yields

$$T_2 = p_2/p_1 * T_1 = 500atm/50atm * 300K = 3000K$$

we find the answer to be 3000 K.

The law of combining volumes was interpreted by the Italian chemist Amedeo Avogadro in 1811, using what was then known as the Avogadro hypothesis. We would now properly refer to it as Avogadro's law:

Equal volumes of gases under the same conditions of temperature and pressure contain equal numbers of molecules.

This can be understood in the following. As in an ideal gas, all molecules are considered to be tiny particles with no spatial extension which collide elastically with each other. So, the kind of gas is irrelevant. Avogadro found that at room temperature, in atmospheric pressure the volume of a mol of a substance, i.e. $6.022 \cdot 10^{23}$ molecules or atoms, occupies the volume of 22.4 l.

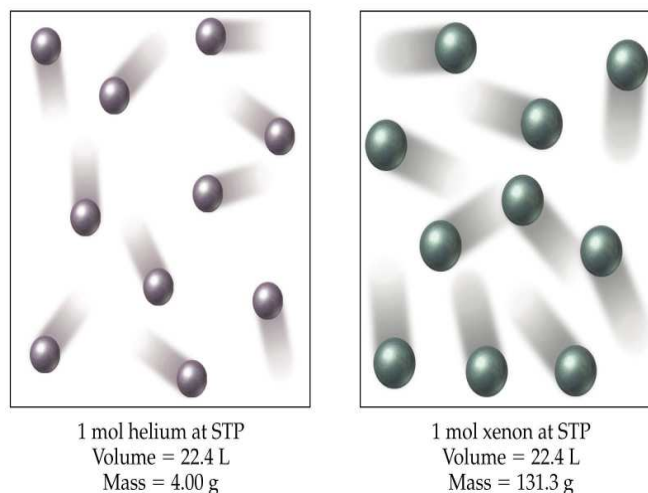


Figure 1.8: Two different gases occupying the same volume under the same circumstances.

Combination of the three empirical gas laws, described in the preceding three sections leads to the **Ideal Gas Law** which is usually written as:

$$p \cdot V = n \cdot R \cdot T \tag{1.2}$$

where p = pressure, V = volume, n = number of mols, T = kelvin temperature and R the ideal gas constant.

The ideal gas constant R in this equation is known as the universal gas constant. It arises from a combination of the proportionality constants in the three empirical gas laws. The universal gas constant has a value which depends only upon the units in which the pressure and volume are measured. The best available value of the universal gas constant is:

$$8.3143510 \frac{\text{J}}{\text{molK}} \text{ or } 8.3143510 \frac{\text{kPa dm}^3}{\text{molK}}$$

Another value which is sometimes convenient is $0.08206 \text{ dm}^3 \text{ atm/mol K}$. R is related to the Boltzmann-constant as:

$$R = N_0 \cdot k_B \quad (1.3)$$

where N_0 is the number of molecules in a mol of a substance, i.e. $6.022 \cdot 10^{23}$ and k_B is $1.308 \cdot 10^{-23} \text{ J/K}$ is valid for one single particle.

This ideal gas equation is one of the most used equations in daily life, which we show in the following problem set:

Worked Example 6

ideal gas 1

A sample of 1.00 mol of oxygen at $50 \text{ }^\circ\text{C}$ and 98.6 kPa occupies what volume?

Solution:

We solve the ideal gas equation for the volume

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

and plug in the values $n = 1$, $T = 273.15 + 50 \text{ K} = 323.15 \text{ K}$ and $p = 98.6 \cdot 10^3 \text{ Pa}$, yielding for the volume $V = 0.0272 \text{ m}^3 = 27.2 \text{ dm}^3$.

This equation is often used to determine the molecular masses from gas data.

Worked Example 7

ideal gas 2

A liquid can be decomposed by electricity into two gases. In one experiment, one of the gases was collected. The sample had a mass of 1.090 g , a volume of 850 ml , a pressure of 746 torr , and a temperature of $25 \text{ }^\circ\text{C}$. Calculate its molecular mass.

Solution:

To calculate the molecular mass we need the number of grams and the number of mols. We can get the number of grams directly from the information in the question. We can calculate the mols from the rest of the information and the ideal gas equation.

$$V = 850\text{mL} = 0.850\text{L} = 0.850\text{dm}^3$$

$$P = 746\text{torr}/760\text{torr} = 0.982\text{atm}$$

$$T = 25.0^\circ\text{C} + 273.15 = 298.15\text{K}$$

$$pV = nRT$$

$$(0.982\text{atm})(0.850\text{L}) = (n)(0.0821\text{Latmmol}^{-1}\text{K}^{-1})(298.15\text{K})$$

$$n = 0.0341\text{mol}$$

molecular mass = g/mol = 1.090 g / 0.0341 mol = 31.96 g/mol. The gas is oxygen.

Or the equation can be comfortably used to design a gas temperature controller:

Worked Example 8

ideal gas 3

In a gas thermometer, the pressure needed to fix the volume of 0.20 g of Helium at 0.50 L is 113.3 kPa. What is the temperature?

Solution:

We transform first need to find the number of mols for Helium. Helium consists of 2 protons and 2 neutrons in the core (see later) and therefore has a molar volume of 4 g/mol. Therefore, we find

$$n = 0.20\text{g}/4\text{g/mol} = 0.05\text{mol}$$

plugging this into the ideal gas equation and solving for the temperature T we find:

$$T = \frac{pV}{nR} = \frac{113.3 \cdot 10^3\text{Pa} \cdot 0.5 \cdot 10^{-3}\text{m}^3}{0.05\text{mol} \cdot 8.314\text{J/molK}} = 136.3\text{K}$$

The temperature is 136 Kelvin.

1.4.2 Kinetic theory of gasses

Any scientific law is an empirical generalization which describes the results of several experiments. A law, however, only describes results; it does not explain why they have been obtained. A theory is a description which explains the results of experiments. The kinetic-molecular theory of gases is a theory of great explanatory power. We shall see how it explains the ideal gas law, which includes the laws of Boyle and of Charles; Dalton's law of partial pressures; and the law of combining volumes.

The kinetic-molecular theory of gases can be stated as four postulates:

- A gas consists of particles (atoms or molecules) in continuous, random motion.
- Gas molecules influence each other only by collision; they exert no other forces on each other.
- All collisions between gas molecules are perfectly elastic; all kinetic energy is conserved.
- The average energy of translational motion of a gas particle is directly proportional to temperature.

In addition to the postulates above, it is assumed that the volumes of the particles are negligible as compared to container volume.

These postulates, which correspond to a physical model of a gas much like a group of billiard balls moving around on a billiard table, describe the behavior of an ideal gas. At room temperatures and pressures at or below normal atmospheric pressure, real gases seem to be accurately described by these postulates, and the consequences of this model correspond to the empirical gas laws in a quantitative way.

We define the average kinetic energy of translation E_t of a particle in a gas as

$$E_t = 1/2 \cdot mv^2 \quad (1.4)$$

where m is the mass of the particle with average velocity v . The fourth postulate states that the average kinetic energy is a constant defining the temperature, i.e. we can formulate

$$E_t = 1/2 \cdot mv^2 = c \cdot T \quad (1.5)$$

where the temperature T is given in Kelvin and c is a constant, which has the same value for all gases. As we have 3 different directions of motion and each possible movement gives $k_B T$, we find for the energy of a particle in a gas as

$$E_t = 1/2 \cdot mv^2 = 3/2 k_B T = 3/2 \frac{R}{N_A} T \quad (1.6)$$

Hence, we can find an individual gas particle's speed rms = root mean square, which is the average square root of the speed of the individual particles (find u)

$$v_{rms} = \sqrt{\frac{3RT}{M_{mol}}} \quad (1.7)$$

where M_{mol} is the molar mass, i.e. the mass of the particle m times the Avogadro number N_A .

Worked Example 9

kinetic theory 1

Calculate the root-mean-square velocity of oxygen molecules at room temperature, 25 °C.

Solution:

Using

$$v_{rms} = \sqrt{3RT/M_{mol}} \quad ,$$

the molar mass of molecular oxygen is 31.9998 g/mol; the molar gas constant has the value 8.3143 J/mol K, and the temperature is 298.15 K. Since the joule is the $\text{kg}\cdot\text{m}^2\cdot\text{s}^{-2}$, the molar mass must be expressed as 0.0319998 kg/mol. The root-mean-square velocity is then given by:

$$v_{rms} = \sqrt{3(8.3143)(298.15)/(0.0319998)} = 482.1\text{m/s}$$

A speed of 482.1 m/s is 1726 km/h, much faster than a jetliner can fly and faster than most rifle bullets.

The very high speed of gas molecules under normal room conditions would indicate that a gas molecule would travel across a room almost instantly. In fact, gas molecules do not do so. If a small sample of the very odorous (and poisonous!) gas hydrogen sulfide is released in one corner of a room, our noses will not detect it in another corner of the room for several minutes unless the air is vigorously stirred by a mechanical fan. The slow diffusion of gas molecules which are moving very quickly occurs because the gas molecules travel only short distances in straight lines before they are deflected in a new direction by collision with other gas molecules.

The distance any single molecule travels between collisions will vary from very short to very long distances, but the average distance that a molecule travels between collisions in a gas can be calculated. This distance is called the *mean free path* l of the gas molecules. If the root-mean-square velocity is divided by the mean free path of the gas molecules, the result will be the number of collisions one molecule undergoes per second. This number is called the *collision frequency* Z_1 of the gas molecules.

The postulates of the kinetic-molecular theory of gases permit the calculation of the mean free path of gas molecules. The gas molecules are visualized as small hard spheres. A sphere of diameter d sweeps through a cylinder of cross-sectional

area $\pi \cdot (d/2)^2$ and length v_{rms} each second, colliding with all molecules in the cylinder.

The radius of the end of the cylinder is d because two molecules will collide if their diameters overlap at all. This description of collisions with stationary gas molecules is not quite accurate, however, because the gas molecules are all moving relative to each other. Those relative velocities range between zero for two molecules moving in the same direction and $2v_{rms}$ for a head-on collision. The average relative velocity is that of a collision at right angles, which is $\sqrt{2}v_{rms}$. The total number of collisions per second per unit volume, Z_1 , is

$$Z_1 = \pi d^2 \sqrt{2} v_{rms} \quad (1.8)$$

This total number of collisions must now be divided by the number of molecules which are present per unit volume. The number of gas molecules present per unit volume is found by rearrangement of the ideal gas law to $n/V = p/RT$ and use of Avogadro's number, $n = N/N_A$; thus $N/V = pN_A/RT$. This gives the mean free path of the gas molecules, l , as

$$(u_{rms}/Z_1)/(N/V) = l = RT/\pi d^2 p N_A \sqrt{2} \quad (1.9)$$

According to this expression, the mean free path of the molecules should get longer as the temperature increases; as the pressure decreases; and as the size of the molecules decreases.

Worked Example 10

mean free path

Calculate the length of the mean free path of oxygen molecules at room temperature, 25 °C, taking the molecular diameter of an oxygen molecule as 370 pm.

Solution:

Using the formula for mean free path given above and the value of the root-mean-square velocity u_{rms} ,

$$l = \frac{(8.3143 \text{ kg m}^2 \text{ s}^{-2} / \text{K mol})(298.15 \text{ K})}{\pi (370 \cdot 10^{-12} \text{ m})^2 (101325 \text{ kg/m.s}^2) (6.0225 \cdot 10^{23} \text{ mol}^{-1}) \sqrt{2}},$$

$$\text{so } l = 6.7 \cdot 10^{-8} \text{ m} = 67 \text{ nm.}$$

The apparently slow diffusion of gas molecules takes place because the molecules travel only a very short distance before colliding. At room temperature and atmospheric pressure, oxygen molecules travel only $(6.7 \cdot 10^{-8} \text{ m}) / (370 \cdot 10^{-12} \text{ m}) = 180$ molecular diameters between collisions. The same thing can be pointed out using the collision frequency for a single molecule Z_1 , which is the root-mean-square velocity divided by the mean free path:

$$Z_1 = \frac{\pi d^2 p N_A \sqrt{2}}{RT} = v_{rms}/l \quad (1.10)$$

For oxygen at room temperature, each gas molecule collides with another every 0.13 nanoseconds (one nanosecond is $1.0 \cdot 10^{-9}$ s), since the collision frequency is $7.2 \cdot 10^{+9}$ collisions per second per molecule.

For an ideal gas, the number of molecules per unit volume is given using $pV = nRT$ and $n = N/N_A$ as

$$N/V = N_A p / RT \quad (1.11)$$

which for oxygen at 25 °C would be $(6.022 \cdot 10^{23} \text{ mol}^{-1})(101325 \text{ kg/m s}^2) / (8.3143 \text{ kg m}^2/\text{s}^2 \text{ K mol})(298.15 \text{ K})$ or $2.46 \cdot 10^{25}$ molecules/m³. The number of collisions between two molecules in a volume, Z_{11} , would then be the product of the number of collisions each molecule makes times the number of molecules there are, $Z_1 N/V$, except that this would count each collision twice (since two molecules are involved in each one collision). The correct equation must be

$$Z_{11} = \frac{\pi d^2 p^2 N_A^2 \sqrt{2} v_{rms}}{2R^2 T^2} \quad (1.12)$$

If the molecules present in the gas had different masses they would also have different speeds, so an average value of v_{rms} would be using a weighted average of the molar masses; the partial pressures of the different gases in the mixture would also be required. Although such calculations involve no new principles, they are beyond our scope.

1.4.3 Pressure of a gas

In the kinetic-molecular theory of gases, pressure is the force exerted against the wall of a container by the continual collision of molecules against it. From Newton's second law of motion, the force exerted on a wall by a single gas molecule of mass m and velocity v colliding with it is:

$$F = m \cdot a = m \frac{\delta v}{\delta t} \quad (1.13)$$

In the above equation, the change in a quantity is indicated by the symbol δ , that means by changing the time t by a fraction, we change the velocity v by some other minimal amount. It is assumed that the molecule rebounds *elastically* and *no kinetic energy is lost* in a perpendicular collision, so $\delta v = v - (-v) = 2v$ (see figure below). If the molecule is moving perpendicular to the wall it will strike the opposite parallel wall, rebound, and return to strike the original wall again. If the length of the container or distance between the two walls is the path length l , then the time between two successive collisions on the same wall is $\delta t = 2l/v$. The continuous force which the molecule moving perpendicular to the wall exerts is therefore

$$F = m \frac{2v}{2l/v} = \frac{mv^2}{l} \quad (1.14)$$

The molecules in a sample of gas are not, of course, all moving perpendicularly to a wall, but the components of their actual movement can be considered

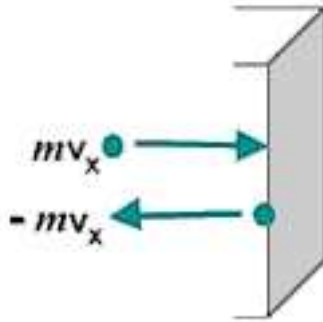


Figure 1.9: Change in momentum as a particle hits a wall.

to be along the three mutually perpendicular x , y , and z axes. If the number of molecules moving randomly, N , is large, then on the average one-third of them can be considered as exerting their force along each of the three perpendicular axes. The square of the average velocity along each axis, $v^2(x)$, $v^2(y)$, or $v^2(z)$, will be one-third of the square of the average total velocity v^2 :

$$v^2(x) = v^2(y) = v^2(z) = v^2/3 \quad (1.15)$$

The average or mean of the square of the total velocity can replace the square of the perpendicular velocity, and so for a large number of molecules N ,

$$F = (N/3) \frac{mv^2}{t} \quad (1.16)$$

Since pressure is force per unit area, and the area of one side of a cubic container must be l^2 , the pressure p will be given by F/l^2 as:

$$p = (N/3) \frac{mv^2}{l^3} \quad (1.17)$$

This equation rearranges to

$$pV = N \cdot mv^2/3 \quad (1.18)$$

because volume V is the cube of the length l . The form of the ideal gas law given above shows the pressure-volume product is directly proportional to the mean-square velocity of the gas molecules. If the velocity of the molecules is a function only of the temperature, and we shall see in the next section that this is so, the kinetic-molecular theory gives a quantitative explanation of Boyle's law.

Worked Example 11

gas pressure

A square box contains He (Helium) at 25 °C. If the atoms are colliding with the walls perpendicularly (at 90°) at the rate of $4.0 \cdot 10^{22}$

times per second, calculate the force (in Newtons) and the pressure exerted on the wall per mol of He given that the area of the wall is 100 cm^2 and the speed of the atoms is 600 ms^{-1} .

Solution:

We use the equation 1.16 to calculate the force.

$$F = (N/3) \frac{mv^2}{l} = (N/3)mv \frac{v}{l}$$

The fraction v/l is the collision frequency $Z_1 = 0.6679 \text{ s}^{-1}$. The product of $N \cdot Z_1$ is the number of molecules impinging on the wall per second. This induces for the force:

$$F = (N/3)mv\tau = 6.022 \cdot 10^{23}/3 \cdot \frac{0.004 \text{ g/mol}}{6.022 \cdot 10^{23}} \cdot 600 \text{ m/s} \cdot 0.6679 \text{ s}^{-1}$$

yielding for the force $F = 0.534 \text{ N}$. The pressure is the force per area:

$$p = F/A = 0.534 \text{ N}/0.01 \text{ m}^2 = 53.4 \text{ Pa}.$$

The calculated force is 0.534 N and the resulting pressure is 53.4 Pa .

1.4.4 Kinetic energy of molecules

In the following, we will make the connection between the kinetic theory and the ideal gas laws. We will find that the temperature is an important quantity which is the only intrinsic parameter entering in the kinetic energy of a gas.

We will consider an ensemble of molecules in a gas, where the molecules will be regarded as rigid large particles. We therefore neglect any vibrations or rotations in the molecule. Hence, making this assumption, Physics for a molecular gas is the same as for a single atom gas.

The square of the velocity is sometimes difficult to conceive, but an alternative statement can be given in terms of kinetic energy. The kinetic energy E_k of a single particle of mass m moving at velocity v is $mv^2/2$. For a large number of molecules N , the total kinetic energy E_k will depend on the mean-square velocity in the same way:

$$E_k = N \cdot mv^2/2 = n \cdot Mv^2/2 \quad (1.19)$$

The second form is on a molar basis, since $n = N/N_A$ and the molar mass $M = mN_A$ where N_A is Avogadro's number $6.022 \cdot 10^{23}$. The ideal gas law then appears in the form:

$$pV = 2E_k/3 \quad (1.20)$$

Compare $pV = nMv^2/2$. This statement that the pressure-volume product of an ideal gas is directly proportional to the total kinetic energy of the gas is also a statement of Boyle's law, since the total kinetic energy of an ideal gas depends only upon the temperature.

Comparison of the ideal gas law, $pV = nRT$, with the kinetic-molecular theory expression $pV = 2E_k/3$ derived in the previous section shows that the total kinetic energy of a collection of gas molecules is directly proportional to the absolute temperature of the gas. Equating the pV term of both equations gives

$$E_k = 3/2nRT \quad , \quad (1.21)$$

which rearranges to an explicit expression for temperature,

$$T = \frac{2}{3R} \frac{E_k}{n} = \frac{Mv^2}{3R} \quad (1.22)$$

We see that temperature is a function only of the mean kinetic energy E_k , the mean molecular velocity v , and the mean molar mass M .

Worked Example 12

mean velocity 1

Calculate the kinetic energy of 1 mol of nitrogen molecules at 300 K?

Solution:

Assume nitrogen behaves as an ideal gas, then

$$E_k = 3/2 \cdot RT = (3/2)8.3145J/(molK) \cdot 300K = 3742J/mol \text{ (or } 3.74kJ/mol \text{)}$$

At 300 K, any gas that behaves like an ideal gas has the same energy per mol.

As the absolute temperature decreases, the kinetic energy must decrease and thus the mean velocity of the molecules must decrease also. At $T = 0$, the absolute zero of temperature, all motion of gas molecules would cease and the pressure would then also be zero. No molecules would be moving. Experimentally, the absolute zero of temperature has never been attained, although modern experiments have extended to temperatures as low as $1 \mu K$.

However, at low temperatures, the interactions between the particles becomes important and we enter a new regime of Quantum Mechanics, which considers molecules, single atoms or protons and electrons simultaneously as waves and as rigid particles. However, this would go too far.

Worked Example 13

mean velocity 2

If the translational rms. speed of the water vapor molecules (H_2O) in air is 648 m/s, what is the translational rms speed of the carbon dioxide molecules (CO_2) in the same air? Both gases are at the same temperature. And what is the temperature we measure?

Solution:

The molar mass of H_2O is

$$M_{\text{H}_2\text{O}} = 2 \cdot 1\text{g/mol} + 1 \cdot 16\text{g/mol} = 18\text{g/mol}$$

As the temperature is constant we can write

$$T = \frac{Mv^2}{3R} = \frac{0.018\text{kg/mol} \cdot (648\text{m/s})^2}{3 \cdot 8.314\text{J/mol} \cdot \text{K}} = 303.0\text{K} = 29.9^\circ\text{C}$$

Now we calculate the molar mass of CO_2

$$M_{\text{CO}_2} = 2 \cdot 16\text{g/mol} + 1 \cdot 12\text{g/mol} = 44\text{g/mol}$$

The rms velocity is again calculated with eq. 1.22

$$v_{\text{CO}_2} = \sqrt{3 \frac{R \cdot T}{M_{\text{CO}_2}}} = \sqrt{\frac{3 \cdot 8.314\text{J/molK} \cdot 303.0\text{K}}{0.044\text{kg/mol}}} = 414.5\text{m/s}$$

The experiment was performed at 29.9°C and the speed of the CO_2 -molecules is 414.5 m/s, that is much slower than the water molecules as they are much heavier.

1.5 Temperature

1.5.1 Thermal equilibrium

1.5.2 Temperature scales

1.5.3 Practical thermometers

1.6 Thermal Properties of Materials

1.6.1 Specific heat capacity

Conversion of macroscopic energy to microscopic kinetic energy thus tends to raise the temperature, while the reverse conversion lowers it. It is easy to show experimentally that the amount of heating needed to change the temperature of a body by some amount is proportional to the amount of matter in the body. Thus, it is natural to write

$$\Delta Q = MC\Delta T$$

(23.4)

where M is the mass of material, ΔQ is the amount of energy transferred to the material, and ΔT is the change of the material's temperature. The quantity

C is called the specific heat of the material in question and is the amount of energy needed to raise the temperature of a unit mass of material one degree in temperature. C varies with the type of material. Values for common materials are given in table 22.2.

Table 22.2: Specific heats of common materials. Material C ($\text{J kg}^{-1} \text{K}^{-1}$)
 brass 385 glass 669 ice 2092 steel 448 methyl alcohol 2510 glycerine 2427 water
 4184

1.6.2 Specific latent heat

It can be seen that the specific heat as defined above will be infinitely large for a phase change, where heat is transferred without any change in temperature. Thus, it is much more useful to define a quantity called latent heat, which is the amount of energy required to change the phase of a unit mass of a substance at the phase change temperature.

1.6.3 Internal energy

In thermodynamics, the internal energy is the energy of a system due to its temperature. The statement of first law refers to thermodynamic cycles. Using the concept of internal energy it is possible to state the first law for a non-cyclic process. Since the first law is another way of stating the conservation of energy, the energy of the system is the sum of the heat and work input, i.e., $E = Q + W$. Here E represents the heat energy of the system along with the kinetic energy and the potential energy ($E = U + \text{K.E.} + \text{P.E.}$) and is called the total internal energy of the system. This is the statement of the first law for non-cyclic processes.

For gases, the value of K.E. and P.E. is quite small, so the important internal energy function is U . In particular, since for an ideal gas the state can be specified using two variables, the state variable u is given by $u = cv + \frac{R}{M}t$, where v is the specific volume and t is the temperature. Thus, by definition, $du = cv dt$, where cv is the specific heat at constant volume.

Internal energy of an Ideal gas

In the previous section, the internal energy of an ideal gas was shown to be a function of both the volume and temperature. Joule performed an experiment where a gas at high pressure inside a bath at the same temperature was allowed to expand into a larger volume.

picture required

In the above image, two vessels, labeled A and B, are immersed in an insulated tank containing water. A thermometer is used to measure the temperature of the water in the tank. The two vessels A and B are connected by a tube, the flow through which is controlled by a stop. Initially, A contains gas at high pressure, while B is nearly empty. The stop is removed so that the vessels are connected and the final temperature of the bath is noted.

The temperature of the bath was unchanged at the end of the process, showing that the internal energy of an ideal gas was the function of temperature alone. Thus Joule's law is stated as $du = cv dt$.

1.6.4 First law of thermodynamics

We now address some questions of terminology. The use of the terms “heat” and “quantity of heat” to indicate the amount of microscopic kinetic energy inhabiting a body has long been out of favor due to their association with the discredited “caloric” theory of heat. Instead, we use the term internal energy to describe the amount of microscopic energy in a body. The word heat is most correctly used only as a verb, e. g., “to heat the house”. Heat thus represents the transfer of internal energy from one body to another or conversion of some other form of energy to internal energy. Taking into account these definitions, we can express the idea of energy conservation in some material body by the equation

$$\Delta E = \Delta Q - \Delta W \quad (\text{first law of thermodynamics})$$

where ΔE is the change in internal energy resulting from the addition of heat ΔQ to the body and the work ΔW done by the body on the outside world. This equation expresses the first law of thermodynamics. Note that the sign conventions are inconsistent as to the direction of energy flow. However, these conventions result from thinking about heat engines, i. e., machines which take in heat and put out macroscopic work. Examples of heat engines are steam engines, coal and nuclear power plants, the engine in your automobile, and the engines on jet aircraft.

1.7 Important Equations and Quantities

Units				
Quantity	Symbol	Unit	S.I. Units	Direction
			or	

Table 1.1: Units used in **Electricity and Magnetism**