Chapter 1

Heat and Properties of Matter

1.1 Properties 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.

$$\rho = \frac{m}{V} \quad , \quad density = \frac{Mass}{Volume}$$

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 steal 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:

volume = Length * Width * Height

For Aluminum: $volume = 2cm * 3cm * 5cm = 30cm^3$ For Lead: $volume = 3cm * 3cm * 5cm = 45cm^3$

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

For Aluminum: $density = \frac{81g}{30cm^3} = 2.7g/cm^3$ For Lead: $density = \frac{510.3g}{45cm^3} = 11.34g/cm^3$ 3cm

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. In nature, a material can be found in various phases, such as water can be liquid, ice or vapor. This can only be understood within the theory of thermodynamics. Thermodynamics deals with quantities, such as:

- Internal energy: U : sum of kinetic and potential energy
- Entropy: S : measure for the disorder in a system
- Free Energy: F : measures the energy of the total state

The free energy is the difference between the inner energy U minus the temperature T multiplied by the entropy S.

$$F = U - T \cdot S \tag{1.1}$$

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 F is a continuous well-behaved function of external conditions such as temperature or pressure. At certain conditions, the stable state is the one which minimizes the free energy.

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.

$$S = \frac{\delta F}{\delta T} \tag{1.2}$$

1.2.1 Solids

From equation 1.1 we see that at low temperatures, the term U dominates, that is, we want the kinetic and potential energies to be low, which is realized in solids.

Solids are materials in which the atoms or molecules are set in place. We distinguish different types of solids: The most disordered solids are the *amorphous solids*, like glass or various plastic materials, where the material is hard but on the other hand, the atoms are not completely ordered. In *ionic crystals* such as table salt crystals NaCl, one type of atoms gives one or more electrons to another atom, and hence charging itself. These *ions* are connected to their neighbors by electrical attraction. *Covalently bonded crystals* such as aluminium, iron, silicon or diamond

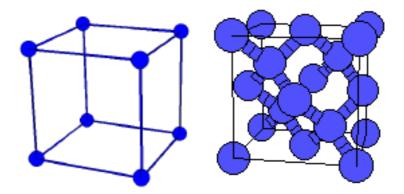


Figure 1.1: Two different crystal structures. The left side shows a simple cubic structure as appears for NaCl, whereas the right side shows the crystal structure of diamond or Silicon.

produce the hardest materials. In the last two classes, crystalline solids, the atoms are arranged on a lattice. Two different lattices are shown in fig. 1.2.1 for the most simple crystal as realized in NaCl or a more complicated for diamond or silicon. At first sight, one cannot distinguish among the various forms of lattices. One can determine the structure of a material by irradiating X-ray light.

Worked Example 3

X-ray light

As a side project: As we know, light can be described as a wave. Find out the frequency range for X-rays. From that calculate the range of wave lengths λ . Find out in the internet the ionic radii for Na and Cl. Calculate an average size of the lattice spacing *a* for NaCl.

Solution:

The frequency ν range for X-rays is given between approximately

$$6.0 \cdot 10^{16} s^{-1} < \nu < 1.0 \cdot 10^{20} s^{-1}$$

With the relation $\lambda = c/\nu$ we obtain for the range of wave lengths λ

$$3.0 \cdot 10^{-3} nm < \lambda < 50 nm$$

A good table of characteristics for all elements is given on http://www.webelements.com/. The atomic radius for Na is $r_{Na} \approx 0.190$ nm, the one for Cl is $r_{Cl} \approx 0.08$ nm. At first sight one would estimate the size of the lattice parameter to be 0.27 nm. This is however too small, as the electric charges repel each other. It is approximately 0.45 nm.

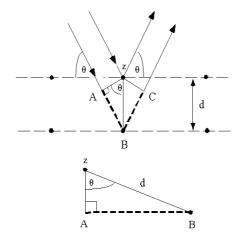


Figure 1.2: Explanation of Bragg's law. Two incident X-rays are reflected by the planes. The triangles denote the necessary conditions for constructive interference.

Lets consider the arrangement on fig. 1.2.1. An X-ray which reflects from the surface of a substance has travelled less distance than an X-ray which reflects from a plane of atoms inside the crystal, on the next plane. The penetrating X-ray travels down to the internal layer, reflects, and travels back over the same distance before being back at the surface. The conditions necessary is to make the phases of the beams coincide when the incident angle equals and reflecting angle. The rays of the incident beam are always in phase and parallel up to the point at which the top beam strikes the top layer at atom z. The second beam continues to the next layer where it is scattered by atom B. The second beam must travel the extra distance AB + BC if the two beams are to continue traveling adjacent and parallel. This extra distance must be an integral n multiple of the wave length λ for the phases of the two beams to be the same: $n\lambda = AB + BC$.

Recognizing d as the hypotenuse of the right triangle ABz, we can use trigonometry to relate d and q to the distance (AB + BC). The distance AB is opposite q so, AB = d sin(q).

Because AB = BC, $n\lambda = 2AB$. Bragg recognized these geometries first and expressed this in an equation now known as *Bragg's Law*:

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta) \tag{1.3}$$

Worked Example 4

Bragg's Law

Given $\lambda = 100$ pm, and knowing that for the Pyrolytic Graphite the distance between the layers is d = 3 Å, use Bragg's law to determine the correct Bragg angle for the first reflection.

Solution:

We will simply use Bragg's law and solve for θ

$$\theta = \arcsin\left(\frac{n \cdot \lambda}{2 \cdot d}\right)$$

This gives for the first Bragg angle: $\theta = 9.6^{\circ}$.

The temperature that can be shown by solid materials is due to the movement in place of the atoms or molecules. They have no independent linear motion of translation because they are attached to one another. Solids can have molecular energy due to vibration and rotation. Picture a class of second graders glued to their seat. Each student can jump up and down and sideways and turn the chair around, but they cant move out of place. Another useful mental picture is a junkyard for springs. The springs have all been tied to each other in one enormous mass. Each spring can twist and vibrate, but it cant get loose from its neighbor.

It is now necessary to change from being able to see and understand each atom or molecule to our larger world. Solids show a definite shape and a definite volume. Unless forces are used that are not commonly found near the earths surface, solids have a very low compressibility.

1.2.2 Deformation of solids

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.

$$stress = rac{Force}{Area_{crosssection}} \implies \sigma = rac{F}{A}$$

(A) Banderderontepseesion

Figure 1.3: 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 1.4: 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:

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

 ΔL

Figure 1.5: Left end of bar is fixed as length changes

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

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

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.

Figure 1.6: dashed line represents plastic recovery **incomplete**

Figure 1.7: dashed line represents plastic recovery **incomplete**

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.

1.2.3 Liquids

Liquids are materials in which the atoms or molecules are as close to each other as solids, but the materials can slip over each other to change places. If you were only a few magnitudes larger than atoms, you might view liquids as B-Bs in a dump truck. Consider a large dump truck going fast down a very bumpy road. The B-Bs have some energy from the bumpy road. The top of the load is level. A few B-Bs are always in the process of getting enough energy to hop out of the dump truck. (This is a picture of vapor pressure of a liquid.) The B-Bs can be poured out of the dump truck. If there were a hole in the bottom of the dump truck, the B-Bs would leak out onto the ground. Like the B-Bs, liquids have no shape except for the shape of the container. B-Bs and liquids can not be compressed under common pressures. In a liquid the forces that hold the particles of liquid close to each other are greater than the forces due to motion that would force the particles away from each other.

The property of liquids of incompressibility is useful to us in hydraulic machines. A simple system of automobile hydraulic brakes are a good example of this. The brake pedal pushes a master cylinder. The travel (A description of distance (!) See Units and Measures.) of the brake petal is a few inches. The master cylinder pushes a small area of a liquid (hydraulic fluid) down a small tube (the brake lines) to the wheel cylinders. The wheel cylinders have a much larger area, but they go a shorter distance to push the brake pad against the drum or rotor, depending on what kind of brakes you have. The brake system cannot work correctly if there is any air (gas) in the system because the gas is compressible.

1.2.4 Pressure in fluids

Consider a vessel of liquid as in fig. 1.2.4. The volume is given by

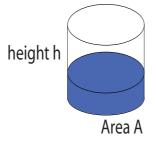


Figure 1.8: Vessel of liquid with area A and height h.

$$V = A \cdot h \tag{1.4}$$

The mass is given by $\rho \cdot V$ as the density is in the whole fluid the same (incompressibility). Therefore the gravitational force on the bottom of the vessel by the fluid is given as

$$F_g = g \cdot \rho Ah \tag{1.5}$$

Therefore, it is easy to see, that the pressure excerted by a fluid with a height h on the bottom and on the walls near the bottom is given as

$$p = \frac{F_g}{A} = \rho g \tag{1.6}$$

and is therefore independent of the form of the vessel. This fact is known as the **hydrostatic paradoxon**.

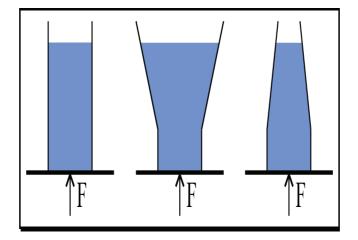
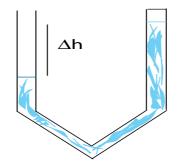


Figure 1.9: Hydrostatic paradoxon

As one sees from the different containers, the pressure is the same for all different vessels. The total pressure in a hydrostatic medium is given as

$$_{ot} = p_0 + \rho gh \tag{1.7}$$

where p_0 is the atmospheric pressure.



 p_t

Figure 1.10: Barometer U-tube.

Worked Example 5

pressureliquid1

Look at fig. 1.2.4. On the right side, the tube is sealed, on the left side it is open to atmospheric pressure. What are the heights for a column of water ($\rho_{water} = 1 \text{ kg/dm}^3$), a column of alcohol ($\rho_{alcohol} = 0.8 \text{ kg/dm}^3$) and a column of mercury ($\rho_{water} = 13.6 \text{ kg/dm}^3$) if the atmospheric pressure is 1 bar? solution

The pressure on the left side is the atmospheric pressure of 10^5 Pa. It is equal to the pressure from the difference of the height of the columns.

$$p_0 = \rho g \Delta h$$

solving for Δh yields for water $\Delta h_{water} = 10.2$ m, for alcohol $\Delta h_{alcohol} = 12.7$ m, and for mercury $\Delta h_{mercury} = 75$ cm. This is the reason that one uses mercury in thermometers. With water the thermometer should be about 10 m long.

In the following, we will meet a force, which is called the buoyant force. As you ascend a solid into a liquid, it might drawn, as in the case of an iron block immersed into water. However, looking at an ice cube, you realize, that it swims in water and some part stays above the surface. Consider in the following the block of solid in the liquid shown in fig. 1.2.4

The top of the cube feels a pressure from the liquid above it given as

$$p_1 = \rho_0 + \rho g h_1 \tag{1.8}$$

whereas on the bottom of the cube there is a pressure on the cube given by

$$p_2 = \rho_0 + \rho g h_2 \tag{1.9}$$

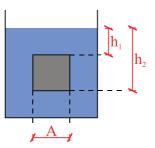


Figure 1.11: buoyant force.

This leads to a difference in pressure and hence to a force $F = p \cdot A$

$$F_{buoyant} = (F_2 - F_1) = A \cdot (p_2 - p_1) = A\rho g(h_2 - h_1) = g \cdot \rho \cdot V_{excluded}$$
(1.10)

We observe that the buoyant force is given by the gravitational force of the solid inside the liquid. If the solid is only partially immersed into a liquid, only the part which is immerse has to be counted for the buoyant force. This is how we can also understand floating or sinking. If the density of a material immersed in a liquid is higher than the one from the material it sinks. If the density is lower, than it floats and only a part is immersed into water.

Worked Example 6

anchor

An iron anchor weighs 1200 kg in air and has a weight density of 8 kg/dm³. If it is immersed in sea water that has a weight density of 1 kg/dm³, how much force would be required to lift it while it is immersed?

solution

The force is given as the sum of the gravitational force mg minus the buoyant force $g\cdot\rho_{water}\cdot V_{anchor}$

$$F = g \cdot \rho_{water} \cdot V_{anchor} - m_{anchor} \cdot g = g \cdot \rho_{water} \cdot \frac{m_{anchor}}{\rho_{anchor}} - m_{anchor} \cdot g \approx 10kN$$

Worked Example 7

ice berg

Why does an ice berg swim in water? *solution*

The density of ice is 0.91 g/cm^3 whereas water has a density of 1 g/cm^3 . Therefore for something which is floating in a liquid, we use the idea, that the gravitational force is equal to the buoyant force. Hence

$$F_{grav} = F_{buoyant}$$

 $mg = gV_{excluded}$

 $\rho_{iceberg} V_{iceberg} g = g \rho_{liquid} V_{immersed}$

$$V_{immersed} = \frac{\rho_{iceberg}}{\rho_{liquid}} V_{iceberg} = 0.91 V_{iceberg}$$

and hence about ninety percent of the ice berg is under the water surface. This can be very dangerous for ships travelling in the north or south seas, since they only see about 10 % of the iceberg.

1.2.5 Fluid mechanics

Fluid mechanics is the study of matter which cannot withstand shear stress. As such, this includes liquids and gases. In our case, fluids are considered a continuous medium which is incompressible. Some fluid mechanics problems can be solved by applying conservation laws (mass, momentum, energy) of mechanics to a finite control volume. However, in general, it is necessary to apply the laws to an infinitesimal control volume. The movement of a tiny volume is characteristic of the movement of the whole liquid. The chapters core is Bernoulli's law and we aim to understand and use it.

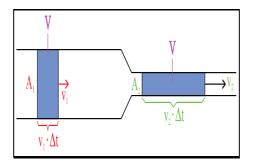


Figure 1.12: The velocity of the fluid is higher in the narrower tube.

In the following we will consider fluids as consisting of small particles with an infinitesimal volume. They move along streamlines. That means, particles arriving at different times at the same position will follow the same path, simply at different times. A streamline is the imaginary line whose tangent gives the velocity of flow at all times. A common practice in analysis is taking some of the walls of a control volume to be along streamlines. Since there is no flow perpendicular to streamlines, only the flow across the other boundaries need be considered. The Italian scientist Giovanni Battista Venturi discovered that the velocity of a fluid in a tube is

inversely proportional to its area. This can be viewed as a consequence of the conservation of mass in an incompressible fluid. Lets say, at a time Δt the fluid that passes point 1 is

$$m_1 = \rho \cdot V_1 = \rho \cdot A_1 \cdot v_1 \cdot \Delta t \tag{1.11}$$

At a point 2, the same mass has to pass there (so write the last equation with index 2). Comparing the two equations yields the equation of conservation of mass (watch, ρ cancels, since it is an incompressible fluid).

$$A_1 \cdot v_1 = A_2 \cdot v_2 \tag{1.12}$$

That means in a thinner tube the velocity has to be higher.

Let us consider a flowing liquid under an external pressure such as the atmosphere. We do not consider any friction here, but say that the liquid can flow without loosing energy and becoming slower. Imagine yourself a tube where the water runs.

The energy of a fractional volume ΔV in this fluid is given as the sum of the kinetic energy

$$E_{kin} = 1/2mv^2 = 1/2\rho V v^2 \tag{1.13}$$

and the potential energy

$$E_{pot} = \rho g h V \tag{1.14}$$

Along a path the total energy is conserved which yields

$$E_{tot}/V = 1/2\rho v^2 + \rho gh \tag{1.15}$$

This finally yields for a fluid on a steady, incompressible flow along a streamline

 $p_0 + \rho gh + 1/2\rho v^2 = constant$ $p_0 : \text{ external pressure } (Pa)$ $\rho : \text{ density } (kgm^{-3})$ $g : 9.81 \ ms^{-2}$ h : height (m) $v : \text{ velociy } (ms^{-2})$

which is a simple but very practical form of the Bernoulli equation. We see that Bernoulli's equation is just the law of conservation of energy without the heat transfer and work.

Worked Example 8

Venturi

Consider fig. 1.2.5. A liquid with density 1 gcm^{-3} moves from left to right. We measure a difference in height of 10 cm. The radius of the second tube is half the radius of the first one. How fast is the liquid moving initially and how fast at the end?

solution

We make use of Bernoulli's equation to see that the pressure difference is

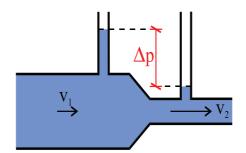


Figure 1.13: The Venturi experiment.

 $\Delta p = 1/2\rho (v_2^2 - v_1^2)$

Using the equation 1.12, we replace v2 and obtain

$$\Delta p = 1/2\rho v_1^2 \left(\frac{A_1^2}{A_2^2} - 1\right)$$

and hence for the initial speed

$$v_1 = \sqrt{\frac{2\Delta p}{\rho\left(\frac{A_1^2}{A_2^2} - 1\right)}} \approx$$

For the final velociy we simply use eq. 1.12 again and obtain $v_2 \approx \dots$.

Worked Example 9

pressureliquid2

A cylinder of 50 cm height filled with water has holes on the side at 10 cm, 20 cm and 30 cm from the bottom of the dewar. Give a drawing of the water coming out of the holes and explain qualitatively how far the water from each hole will reach from the cylinder wall away.

solution

The qualitative solution is given in fig. 1.2.5. At the position h above the dewar we have the pressure

$$p = p_0 + \rho g(50cm - h)$$

This is equal to a pressure from the flow. This gives you for the velocities depending on the height using the Bernoulli equation

$$v = \sqrt{\frac{2}{\rho} [p_0 + \rho g(50cm - h)]}$$

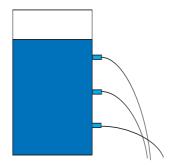


Figure 1.14: pressure in a liquid.

Using the kinetic equations as the liquid is drawn towards the ground by the gravitational force

$$1/2qt^2 = h$$

one solves for the length

$$s = \sqrt{2gh}v$$

And this should yield the behaviour as shown in the fig. 1.2.5.

It may seem that Bernoulli's equation can only be applied in a very limited set of situations, as it requires ideal conditions. However, since the equation applies to streamlines, we can consider a streamline near the area of interest where it is satisfied, and it might still give good results, i.e., you don't need a control volume for the actual analysis (although one is used in the derivation of the equation).

Bernoulli's equation can be rewritten as

$$\frac{p}{\rho g} + \frac{v^2}{2g} + h = constant \tag{1.16}$$

This constant can be called *head of the water*, and is a representation of the amount of work that can be extracted from it. For example, for water in a dam, at the inlet of the penstock, the pressure is high, but the velocity is low, while at the outlet, the pressure is low (atmospheric) while the velocity is high. The value of head calculated above remains constant (ignoring frictional losses).

Let us consider the situation where a fluid passes over a solid body, the streamlines get closer together, the flow velocity increases, and the pressure decreases. Airfoils are designed so that the flow over the top surface is faster than over the bottom surface, and therefore the average pressure over the top surface is less than the average pressure over the bottom surface, and a resultant force due to this pressure difference is produced. This is the source of lift on an airfoil. Lift is defined as the force acting on an airfoil due to its motion, in a direction normal to the direction of motion. Likewise, drag on an airfoil is defined as the force acting on an airfoil due to its motion, along the direction of motion.

An easy demonstration of the lift produced by an airstream requires a piece of notebook paper and two books of about equal thickness. Place the books four to five inches apart, and cover the gap with the paper. When you blow through the passage made by the books and the paper, what do you see? Why?

Two more examples: Example 1 A table tennis ball placed in a vertical air jet becomes suspended in the jet, and it is very stable to small perturbations in any direction. Push the ball down, and it springs back to its equilibrium position; push it sideways, and it rapidly returns to its original position in the center of the jet. In the vertical direction, the weight of the ball is balanced by a force due to pressure differences: the pressure over the rear half of the sphere is lower than over the front half because of losses that occur in the wake (large eddies form in the wake that dissipate a lot of flow energy). To understand the balance of forces in the horizontal direction, you need to know that the jet has its maximum velocity in the center, and the velocity of the jet decreases towards its edges. The ball position is stable because if the ball moves sideways, its outer side moves into a region of lower velocity and higher pressure, whereas its inner side moves closer to the center where the velocity is higher and the pressure is lower. The differences in pressure tend to move the ball back towards the center. Example 3 Suppose a ball is spinning clockwise as it travels through the air from left to right The forces acting on the spinning ball would be the same if it was placed in a stream of air moving from right to left, as shown in fig. 1.2.5.

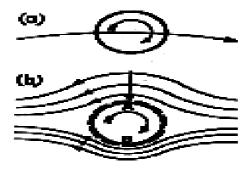


Figure 1.15: The rotating ball.

A thin layer of air (a boundary layer) is forced to spin with the ball because of viscous friction. At A the motion due to spin is opposite to that of the air stream, and therefore near A there is a region of low velocity where the pressure is close to atmospheric. At B, the direction of motion of the boundary layer is the same as that of the external air stream, and since the velocities add, the pressure in this region is below atmospheric. The ball experiences a force acting from A to B, causing its path to curve. If the spin was counterclockwise, the path would have the opposite curvature. The appearance of a side force on a spinning sphere or cylinder is called the Magnus effect, and it well known to all participants in ball sports, especially baseball, cricket and tennis players. Stagnation pressure and dynamic pressure Bernoulli's equation leads to some interesting conclusions regarding the variation of pressure along a streamline. Consider a steady flow impinging on a perpendicular plate (fig. 1.2.5).

There is one streamline that divides the flow in half: above this streamline all the flow goes over the plate, and below this streamline all the flow goes under the plate. Along this dividing streamline, the fluid moves towards the plate. Since the flow cannot pass through the plate, the fluid must come to rest at the point where it meets the plate. In other words, it "stagnates." The fluid along the dividing, or "stagnation streamline" slows down and eventually comes to rest without deflection at the stagnation point.

Bernoulli's equation along the stagnation streamline gives

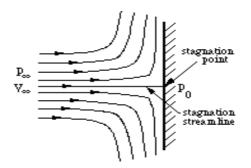


Figure 1.16: Stagnation point flow.

$$p_e + 1/2\rho v_e^2 = p_0 + 1/2\rho v_0^2 \tag{1.17}$$

where the point e is far upstream and point 0 is at the stagnation point. Since the velocity at the stagnation point is zero,

$$p_e + 1/2\rho v_e^2 = p_0 \tag{1.18}$$

The stagnation or total pressure, p_0 , is the pressure measured at the point where the fluid comes to rest. It is the highest pressure found anywhere in the flowfield, and it occurs at the stagnation point. It is the sum of the static pressure (p_0) , and the dynamic pressure measured far upstream. It is called the dynamic pressure because it arises from the motion of the fluid.

The dynamic pressure is not really a pressure at all: it is simply a convenient name for the quantity (half the density times the velocity squared), which represents the decrease in the pressure due to the velocity of the fluid.

We can also express the pressure anywhere in the flow in the form of a non-dimensional pressure coefficient C_p , where

$$C_p = \frac{p-p}{1/2\rho v_e} \tag{1.19}$$

At the stagnation point $C_p = 1$, which is its maximum value. In the freestream, far from the plate, $C_p = 0$. Pitot tube One of the most immediate applications of Bernoulli's equation is in the measurement of velocity with a Pitot-tube. The Pitot tube (named after the French scientist Pitot) is one of the simplest and most useful instruments ever devised. It simply consists of a tube bent at right angles (fig. 1.2.5).

By pointing the tube directly upstream into the flow and measuring the difference between the pressure sensed by the Pitot tube and the pressure of the surrounding air flow, it can give a very accurate measure of the velocity. In fact, it is probably the most accurate method available for measuring flow velocity on a routine basis, and accuracies better than 1% are easily possible. Bernoulli's equation along the streamline that begins far upstream of the tube and comes to rest in the mouth of the Pitot tube shows the Pitot tube measures the stagnation pressure in the flow. Therefore, to find the velocity v_e , we need to know the density of air, and the pressure difference $(p_0 - p_e)$. The density can be found from standard tables if the temperature and the pressure tapping" located on the wall of the wind tunnel, or on the surface of the model.

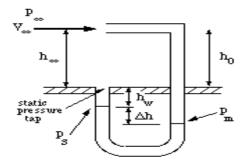


Figure 1.17: The Pitot tube.

1.2.6 gases

Gas, or vapor, is the most energetic phase of matter commonly found here on earth. The particles of gas, either atoms or molecules, have too much energy to settle down attached to each other or to come close to other particles to be attracted by them. Material in the vapor phase have no shape of their own, that is, they take on the shape of the container. Gases have no given volume. A certain amount of gas at a pressure of one atmosphere and a volume of ten liters could become five liters if the pressure was increased or would become more than ten liters if the pressure was decreased.. The gas expands to fill the container. The Gas Law that covers the calculations of the pressure, volume, and temperature of gases is in a later chapter.

How can you picture the materials as a gas? A pool table is only in two dimensions, but what if the balls kept moving and the pool table were in three dimensions? Such a pool table would be like a gas. The rails of the 3-D pool table would be the sides of the container. The billiard balls would bounce off each other in completely elastic collisions and would bounce off the sides of the table to produce a constant pressure. The real hallmark of the gas is that the motion of the particles is so great that the forces of attraction between the particles are not able to hold any of them together.

1.2.7 Phase transitions

The thermodynamic properties of material are described with thermodynamic potentials. Two very important are the free energy F or the entropy S. The free energy depends only on the heat capacity c, where we distinguish the heat capacity per mole of a substance c_{mole} or per kg of a substance c_m . These are usually strongly temperature-dependent quantities. The free energy can be written as

$$F = m \int c_m(T) dT = n \int c_{mole}(T) dT$$
(1.20)

where m is the mass and n the molar mass. In the following we will assume temperatureindependent heat capacities. The change in internal energy as one enhances the temperature is given by $\Delta F = mc_m \Delta T = nc_{mole} \Delta T$ Q : internal energy (J) m : mass (kg) $c_m : \text{heat capacity } (J/kg/K)$ $c_n : \text{molar heat capacity } (J/mole/K)$ T : temperature (K)

Worked Example 10

internal energy

How much energy do you have to put into a vessel containing 1 l of water neglecting the vessel in order to warm it up by 10 degrees? The heat capacity of water is 4182 J/kg/K solution

The solution is simple

$$\Delta F = m * c_m * \Delta T = 1kg * 4182J/kg/K * 10K = 41820J.$$

When a system goes from one phase to another, there will generally be a region where the system is neither in one phase nor the other. This is known as a phase transition and the regime where the two phases coexist is called the critical regime. Familiar examples of phase transitions are melting (solid to liquid), freezing (liquid to solid), boiling (liquid to gas), and condensation (gas to liquid). A beautiful example where the the two phases coexist is in water, when it starts to boil or when a liquid get opalescent. 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.

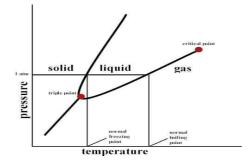


Figure 1.18: The phase diagram of an ordinary material.

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. In fig 1.2.7 we plot a phase diagram of an ordinary substance. At low temperatures, almost any material becomes solid. At ambient pressure it usually transforms into a liquid and increasing the temperature even further, it becomes a gas. If one reduces the pressure, the liquid phase might vanish and there is a transition directly from the solid to the gas-phase.

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.

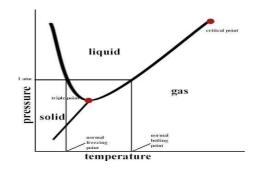


Figure 1.19: The phase diagram of water.

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.

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 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.

1.3 Ideal gasses

Author: Gérald Wigger

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 boiling point, undergoes a transition into a gaseous state. For some materials such as aluminium, one has to heat up to three thousand degrees Celsius (°C), whereas Helium is a gas already at -269 °C. For more examples see Table 1.1. 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. In the following we will be considering often *intensive* versus extensive quantities. A material's intensive property, is a quantity which does not depend on the size of the material, such as temperature, pressure or density. Extensive properties like volume, mass or number of atoms on the other hand gets bigger the bigger the material is (see Table 1.2 for various intensive/extensive properties). If the substance is evenly distributed throughout the volume in question, then a

Material	Temperature in Celsius	Temperature in Kelvin
Aluminium	$2467 \ ^{\circ}\mathrm{C}$	2740 K
Water	$100 \ ^{\circ}\mathrm{C}$	373.15 K
Ethyl alcohol	78.5 °C	351.6 K
Methyl ether	-25 °C	248 K
Nitrogen	-195.8 °C	77.3 K
Helium	-268.9 °C	4.2 K

Table 1.1: Boiling points for various materials in degrees Celsius and in Kelvin

quantity	unit	intensive or extensive	
pressure p	Pa	intensive	
volume V	m^3	extensive	
molar volume v_{mol}	m^3/mol	intensive	
temperature T	Κ	intensive	
mass M	kg	extensive	
density ρ	$\rm kg/m^3$	intensive	
internal energy E	J	extensive	

Table 1.2: Intensive versus extensive properties of matter

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 ideas 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.

1.3.1 Equation of state

The ideal gas can be described with a single equation. However, in order to arrive there, we will be introducing three different equations of state, which lead to the ideal gas law. The combination of these three laws leads to a complete picture of the ideal gas.

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

$$p \cdot V = constant$$

 p : pressure (Pa)
 V : Volume (m³)

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 11

compressed Helium gas

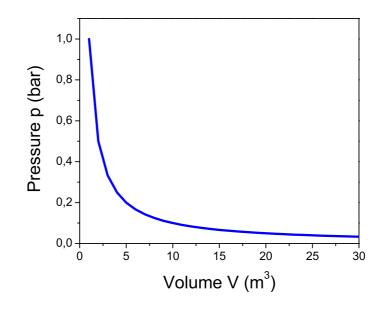


Figure 1.20: Pressure-Volume diagram for the ideal gas at constant temperature.

A sample of Helium gas at 25° C is compressed from 200 cm³ to 0.240 cm³. 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

$$p_1 = p_2 \cdot V_2 / V_1 = 3.00 cm Hg \cdot 0.240 cm^3 / 200 cm^3$$

Setting in the values yields $p_1 = 3.60 \cdot 10^{-3}$ 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. $3.60 \cdot 10^{-3}$ Hg $\cdot 10$ mm/1 cm $= 3.60 \cdot 10^{-2}$ mm Hg $3.60 \cdot 10^{-3}$ Hg $\cdot 1$ atm/76.0 cm Hg $= 4.74 \cdot 10^{-5}$ 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 12

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/m³, $g = 9.81 \text{ ms}^{-2}$.

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:

$$p_1/T_1 = p_2/T_2 = constant$$

 $p_{1,2}$: pressures (Pa)
 $T_{1,2}$: Temperatures (K)

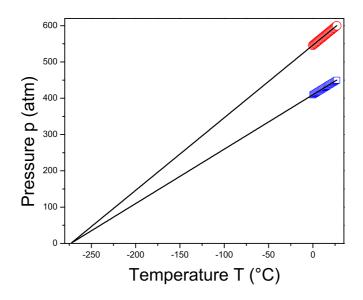


Figure 1.21: Pressure-temperature diagram for the ideal gas at constant volume.

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 K = -273.15 °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.

Worked Example 13

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

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

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.

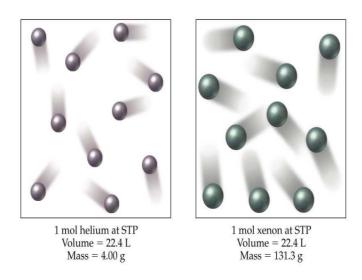


Figure 1.22: Two different gases occupying the same volume under the same circumstances.

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

$$p \cdot V = n \cdot R \cdot T$$

p : pressure (Pa) $V : \text{Volume } (m^3)$ n : number of mols (mol) R : gas konstant (J/molK) T : temperature (K)

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 $\frac{J}{molK}$ or 8.3143510 $\frac{kPadm^3}{molK}$

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

$$R = N_0 \cdot k_B \tag{1.21}$$

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 $1.308 \cdot 10^{-23}$ 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 14

ideal gas 1

A sample of 1.00 mol of oxygen at 50 $^{\circ}\mathrm{C}$ 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 K = 323.15 K and $p = 98.6 \cdot 10^3$ Pa, yielding for the volume V = 0.0272 m³ = 27.2 dm³.

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

Worked Example 15

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 °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.

 $V = 850mL = 0.850L = 0.850dm^{3}$ P = 746torr/760torr = 0.982atm $T = 25.0^{\circ}C + 273.15 = 298.15K$

$$pV = nRT$$

$$(0.982atm)(0.850L) = (n)(0.0821Latmmol - 1K - 1)(298.15K)$$

$$n = 0.0341 mol$$

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 16

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

$$n = 0.20g/4g/mol = 0.05mol$$

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

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

The temperature is 136 Kelvin.

1.3.2 Kinetic theory of gasses

The results of several experiments can lead to a *scientific law*, which describes then all experiments performed. This is an empirical, that is based on experience only, approach to Physics. A law, however, only describes results; it does not explain why they have been obtained. Significantly stronger, a *theory* is a formulation which explains the results of experiments. A theory usually bases on *postulates*, that is a proposition that is accepted as true in order to provide a basis for logical reasoning. The most famous postulate in Physics is probably the one formulated by Walter Nernst which states that if one could reach absolute zero, all bodies would have the same entropy.

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

$$E_t = 1/2 \cdot mv^2 \tag{1.22}$$

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

$$E_t = 1/2 \cdot mv^2 = c \cdot T \tag{1.23}$$

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_BT , we find for the energy of a particle in a gas as

$$E_t = 1/2 \cdot mv^2 = 3/2k_BT = 3/2\frac{R}{N_A}T \tag{1.24}$$

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)

$$v_{rms} = \sqrt{\frac{3RT}{M_{mol}}} \tag{1.25}$$

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

Worked Example 17

kinetic theory 1

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

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

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 kg·m²·s⁻², the molar mass must be expressed as 0.0319998 kg/mol. The root-mean-square velocity is then given by:

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

A speed of 482.1 m/s is 1726 km/h, much faster than a jet liner 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

$$Z_1 = \pi d^2 \sqrt{2} v_{rms} \tag{1.26}$$

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

$$(u_{rms}/Z_1)/(N/V) = l = RT/\pi d^2 p N_A \sqrt{2}$$
(1.27)

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 18

mean free path

Calculate the length of the mean free path of oxygen molecules at room temperature, 25 $^{\circ}$ 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} ,

$$l = \frac{(8.3143 kgm^2 s^{-2}/Kmol)(298.15K)}{\pi (370 \cdot 10^{-12}m)2(101325 kg/ms^2)(6.0225 \cdot 10^{23}mol^{-1})\sqrt{2}},$$
so $l = 6.7 \cdot 10^{-8}$ m = 67 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:

$$Z_1 = \frac{\pi d^2 p N_A \sqrt{2}}{/RT} = v_{rms}/l$$
(1.28)

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

$$N/V = N_A p/RT \tag{1.29}$$

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

$$Z_{11} = \frac{\pi d^2 p^2 N_A^2 \sqrt{2} v_{rms}}{2R^2 T^2} \tag{1.30}$$

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.

1.3.3 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:

$$F = m \cdot a = m \frac{\Delta v}{\Delta t} \tag{1.31}$$

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

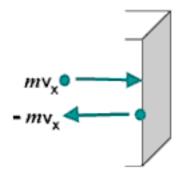


Figure 1.23: Change in momentum as a particle hits a wall.

$$F = m \frac{2v}{2l/v} = \frac{mv^2}{l} \tag{1.32}$$

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 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 :

$$v^{2}(x) = v^{2}(y) = v^{2}(z) = v^{2}/3$$
(1.33)

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,

$$F = (N/3)\frac{mv^2}{l} \tag{1.34}$$

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:

$$p = (N/3)\frac{mv^2}{l^3} \tag{1.35}$$

This equation rearranges to

$$pV = N \cdot mv^2/3 \tag{1.36}$$

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 19

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 cm² and the speed of the atoms is 600 ms⁻¹. Solution:

We use the equation 1.34 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:

$$F = (N/3)mv\tau = 6.022 \cdot 1023/3 \cdot \frac{0.004g/mol}{6.022 \cdot 10^{23}} \cdot 600m/s \cdot 0.6679s^{-1}$$

yielding for the force F = 0.534 N. The pressure is the force per area:

$$p = F/A = 0.534N/0.01m^2 = 53.4Pa.$$

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

1.3.4 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:

$$E_k = N \cdot mv^2 / 2 = n \cdot Mv^2 / 2 \tag{1.37}$$

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:

$$pV = 2E_k/3 \tag{1.38}$$

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 pVterm of both equations gives

$$E_k = 3/2nRT \quad , \tag{1.39}$$

which rearranges to an explicit expression for temperature,

$$T = \frac{2}{3R} \frac{E_k}{n} = \frac{Mv^2}{3R}$$
(1.40)

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 20

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

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

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 μ 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 21

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

$$M_{H_2O} = 2 \cdot 1g/mol + 1 \cdot 16g/mol = 18g/mol$$

As the temperature is constant we can write

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

Now we calculate the molar mass of CO_2

$$M_{CO_2} = 2 \cdot 16g/mol + 1 \cdot 12g/mol = 44g/mol$$

The rms velocity is again calculated with eq. 1.40

$$v_{CO_2} = \sqrt{3\frac{R \cdot T}{M_{CO_2}}} = \sqrt{\frac{3 \cdot 8.314J/molK \cdot 303.0K}{0.044kg/mol}} = 414.5m/s$$

The experiment was performed at 29.9 $^{\circ}$ C and the speed of the CO₂-molecules is 414.5 m/s, that is much slower than the water molecules as they are much heavier.

1.4 Temperature

Let us look back to the equation for the temperature of an ideal gas,

$$T = \frac{2}{3R} \frac{E_k}{n} \tag{1.41}$$

We can see that temperature is proportional to the average kinetic energy of a molecule in the gas. In other words temperature is a measure of how much energy is contained in an object – in hot things the atoms have a lot of kinetic energy, in cold things they have less. It may be surprising that 'hot' and 'cold' are really just words for how fast molecules or atoms are moving around, but it is true.

Definition: Temperature is a measure of the average kinetic energy of the particles in a body.

It should now be clear that heat is nothing more than energy on the move. It can be carried

water

Figure 1.24: A heat flow diagram showing the heat flowing from the warmer water into the cooler ice cube.

by atoms, molecules or electromagnetic radiation but it is always just transport of energy. This is very important when we describe movement of heat as we will do in the following sections. 'Cold' is <u>not</u> a physical thing. It does not move from place to place, it is just the word for a lack of heat, just like dark is the word for an absence of light.

1.4.1 Thermal equilibrium

Now that we have defined the temperature of an isolated object (usually referred to as a body) we need to consider how heat will move between bodies at different temperatures. Let us take two bodies; A which has a fixed temperature and B whose temperature is allowed to change. If we allow heat to move between the two bodies we say they are in thermal contact.

First let us consider what happens if B is cooler than A. Remember – we have fixed the temperture of A so we need only worry about the temperature of B changing. An example of such a situation is an ice cube being dropped into a large pan of boiling water on a fire. The water temperature is fixed i.e. does not change, because the fire keeps it constant. It should be obvious that the ice cube will heat up and melt. In physical terms we say that the heat is flowing out of the (warmer) boiling water, into the (cooler) ice cube. This flow of heat into the ice cube causes it to warm up and melt. In fact the temperature of any cooler object in thermal contact with a warmer one will increase as heat from the warmer object flows into it.

The reverse would be true if B were warmer than A. We can now picture putting a small amount of warm water in to a freezer. If we come back in an hour or so the water will have cooled down and possibly frozen. In physical terms we say that the heat is flowing out of the (warmer) water, into the (cooler) air in the freezer. This flow of heat out of the ice cube in to the aircauses it to cool down and (eventually) freeze. Again, any warm object in thermal contact with a cooler one will cool down due to heat flowing out of it.

There is one special case which we have not yet discussed – what happens if A and B are at the same temperature? In this case B will neither warm up nor cool down, in fact, its temperature will remain constant. When two bodies are at the same temperature we say that they are in thermal equilibrium. Another way to express this is to say that two bodies are in thermal equilibrium if the particles within those bodies have the same average kinetic energies.

water

Figure 1.25: A heat flow diagram showing the heat flowing from the warmer water into the cooler air in the fridge.

Convince yourself that the last three paragraghs are correct before you continue. You should notice that heat always flows from the warmer object to the cooler object, never the other way around. Also, we never talk about coldness moving as it is not a real physical thing, only a lack of heat. Most importantly, it should be clear that the flow of heat between the two objects always attempts to bring them to the same temperature (or in other words, into thermal equilibrium). The logical conclusion of all this is that if two bodies are in thermal contact heat will flow from the hotter object to the cooler one until they are in thermal equilibrium (i.e. at the same temperature). We will see how to deal with this if the temperature of object A is not fixed in the section on heat capacities.

1.4.2 Temperature scales

Temperature scales are often confusing and even university level students can be tricked into using the wrong one. For most purposes in physics we do not use the familiar celcius (often innaccurately called centigrade) scale but the closely related absolute (or kelvin) scale – why? Let us think about the celcius scale now that we have defined temperature as a measure of the average kinteic energy of the atoms or molecules in a body.

A scale is a way of assigning a number to a physical quantity. Consider distance – using a ruler we can measure a distance and find its legnth. This legnth could be measured in metres, inches, or miles. The same is true of temperatures in that many different scales exist to measure them. Table 1.3 shows a few of these scales. Just like a ruler the scales have two defined points which fix the scale (consider the values at the beginning and end of the ruler e.g. 0cm and 15cm). This is usually achieved by defining the temperature of some physical process, e.g. the freezing point of water.

Armed with our knowledge of temperture we can see that Celcius's scale has a big problem – it allows us to have a negative temperature.

$elts = 0^{\circ}F$

Table 1.3: The most important temperature scales.

We found that temperature is a measure of the average kinetic energy of the particles in a body. Therefore, a negative temperature suggests that that the particles have negative kinetic energy. This can not be true as kinetic energy can only be positive. Kelvin addressed this problem by redefining the zero of the scale. He realised that the coldest temperature you could achieve would be when the particles in a body were not moving at all. There is no way to cool something further than this as there is no more kinetic energy to remove from the body. This temperature is called <u>absolute zero</u>. Kelvin chose his scale so that 0K was the same as absolute zero and chose the size of his degree to be the same as one degree in the celcius scale.

Interestingine did a similar thing to Kelvin but set his degree to be the same size as one degree Fact hrenheit. Unfortunately for him, almost everyone preferred Kelvin's absolute scale and the rankine scale is now hardly ever used!

It turns out that the freezing point of water, 0°C, is equal to 273.15 K. So, in order to convert from celcius to kelvin need to subtact 273.15.

Definition: $T(K) = T(^{\circ}C) - 273.15$

1.4.3 Practical thermometers

It is often important to be able to determine an object's temperature precisely. This can be a challenge at very high or low tempertures or in inaccesible places. Consider a scientist who wishes to know how hot the magma in a volcano is. They are not going to be able to just lower a thermometer in to the magma as it will just melt as it reaches the superheated rock.

We will now look at some less extreme situations and show how a variety of thermometry techniques can be developed. Consider first the gas cylinder which we tried to explode in worked example 7 by heating it while sealed. We decided that we would need to heat it to around 3000K before it explodes. How can we check this experimentally? In a sealed gas cylinder the volume of the gas and the number of moles of gas remain constant as we heat, this is why we could use the Gay-Lussac law in example 7. The Gay-Lussac law tells us that pressure is directly proportional

to temperature for fixed volume and amount of gas. Therefore by mesuring the pressure in the cylinder (which can be done by fitting a pressure gauge to the top of it) we can indirectly work out the temperature.

This is similar to familiar alcohol or mercury thermometers. In these we use the fact that expansion of a liquid as it is heated is approximately proportional to temperature so we can use this expansion to as a measure of temperature. In fact, any thermometer you can imagine uses some physical property which varies with temperature to measure it indirectly.

1.4.4 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 (J kg⁻¹ K⁻¹) brass 385 glass 669 ice 2092 steel 448 methyl alcohol 2510 glycerine 2427 water 4184

1.4.5 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.

1.4.6 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 + K.E. + 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 , where v is the specific volume and t is the temperature. Thus, by definition, , 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 and 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 = 0.

1.4.7 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.

1.5 Important Equations and Quantities

Units						
Quantity	Symbol	Unit	S.I. Units	Direction		
			or			

Table 1.4: Units used in Electricity and Magnetism