Properties of Gases

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First year, Hilary term

Suggested Reading

Physical Chemistry, P. W. Atkins
Foundations of Physics for Chemists, G. Ritchie and D. Sivia
Physical Chemistry, W. J. Moore
University Physics, H. Benson

Course synopsis

1.   Introduction - phases of matter
2.   Characteristics of the gas phase
              Examples
              Gases and vapours
3.   Measureable properties of gases
              Pressure
              Measurement of pressure
              Temperature
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10.   Transport properties of gases
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1. Introduction - phases of matter

There are four major phases of matter: solids, liquids, gases and plasmas. Starting from a solid at a temperature below its melting point, we can move through these phases by increasing the temperature. First, we overcome the bonds or intermolecular forces locking the atoms into the solid structure, and the solid melts. At higher temperatures we overcome virtually all of the intermolecular forces and the liquid vapourises to form a gas (depending on the ambient pressure and on the phase diagram of the substance, it is sometimes possible to go directly from the solid to the gas phase in a process known as sublimation). If we increase the temperature to extremely high levels, there is enough energy t:o ionise the substance and we form a plasma. This course is concerned solely with the properties and behaviour of gases. As we shall see, the fact that interactions between gas phase particles are only very weak allows us to use relatively simple models to gain virtually a complete understanding of the gas phase.

2. Characteristics of the gas phase

The gas phase of a substance has the following properties:

1.   A gas is a collection of particles in constant, rapid, random motion (sometimes referred to as 'Brownian' motion). The particles in a gas are constantly undergoing collisions with each other and with the walls of the container, which change their direction − hence the 'random'. If we followed the trajectory of a single particle within a gas, it might look something like the figure on the right.

2.   A gas fills any container it occupies. This is a result of the second law of thermodynamics i.e. gas expanding to fill a container is a spontaneous process due to the accompanying increase in entropy.

3.   The effects of intermolecular forces in a gas are generally fairly small. For many gases over a fairly wide range of temperatures and pressures, it is a reasonable approximation to ignore them entirely. This is the basis of the 'ideal gas' approximation, of which more later.

4.   The physical state of a pure gas (as opposed to a mixture) may be defined by four physical properties:
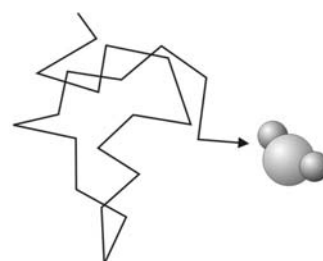
   > p – the pressure of the gas
   > T – the temperature of the gas
   > V – the volume of the gas
   > n – the number of moles of substance present

   In fact, if we know any three of these variables, we can use an *equation of state* for the gas to determine the fourth. Despite the rather grand name, an equation of state is simply an expression that relates these four variables. In Sections 4 and 5, we will consider the equation of state for an ideal gas (one in which the intermolecular forces are assumed to be zero), and we will also look briefly at some models used to describe real (i.e. interacting) gases.

Examples

Elements that are gases at room temperature and atmospheric pressure are He, Ne, Ar, Kr, Xe, Rn (atomic gases) and H_2, O_2, N_2, F_2, Cl_2 (diatomic gases). Other substances that we commonly think of as gases include CO, NO, HCl, O_3, HCN, H_2S, CO_2, N_2O, NO_2, SO_2, NH_3, PH_3, BF_3, SF_6, CH_4, C_2H_6, C_3H_8, C_4H_{10}, CF_2Cl_2. While these substances are all gases at room temperature and pressure, virtually every compound has a gas phase that may be accessed under the appropriate

conditions of temperature and pressure. These conditions may be identified from the phase diagram for the substance.

Gases and vapours

The difference between a 'gas' and a 'vapour' is sometimes a source of confusion. When a gas phase of a substance is present under conditions when the substance would normally be a solid or liquid (e.g. below the boiling point of the substance) then we call this a vapour phase. This is in contrast to a 'fixed gas', which is a gas for which no liquid or solid phase can exist at the temperature of interest (e.g. gases such as N_2, O_2 or He at room temperature).

As an example, at the surface of a liquid there always exists an equilibrium between the liquid and gas phases. At a temperature below the boiling point of the substance, the gas is in fact technically a vapour, and its pressure is known as the 'vapour pressure' of the substance at that temperature. As the temperature is increased, the vapour pressure also increases. The temperature at which the vapour pressure of the substance is equal to the ambient pressure is the boiling point of the substance.

3. Measurable properties of gases

What we mean when we talk about the *amount* of gas present (usually expressed in moles) or the *volume* it occupies is fairly clear. However, the concepts of pressure and temperature deserve a little more discussion.

Pressure

Pressure is a measure of the force exerted by a gas per unit area. Correspondingly, it has SI units of Newtons per square metre (Nm^{-2}), more commonly referred to as Pascals (Pa). Several other units of pressure are in common usage, and conversions between these units and Pascals are given below:

$$1 \text{ Torr} = 1 \text{ mmHg} = 133.3 \text{ Pa}$$
$$1 \text{ bar} = 1000 \text{ mBar} = 100\,000 \text{ Pa}$$

In a gas, the force arises from collisions of the atoms or molecules in the gas with the surface at which the pressure is being measured, often the walls of the container (more on this in Section 7). Note that because the motion of the gas particles is completely random, we could place a surface at any position in a gas and at any orientation, and we would measure the same pressure.

The fact that the measured pressure arises from collisions of individual gas particles with the container walls leads us directly to an important result about mixed gases, namely that the total pressure p exerted by a mixture of gases is simply the sum of the partial pressures p_i of the component gases (the partial pressure p_i is simply the pressure that gas i would exert if it alone occupied the container). This result is known as Dalton's law.

$$p = \Sigma_i \, p_i \qquad\qquad \text{Dalton's law} \qquad (3.1)$$

Measurement of pressure

Pressure measurement presents a challenge in that there is no single physical effect that can be used over the entire range from extremely low to extremely high pressure. As we shall see, many ingenious methods have been devised for measuring pressure. At pressures higher than about 10^{-4} mbar, gauges based on mechanical phenomena may be used. These work by measuring the actual force exerted by the gas in a variety of ways, and provide an absolute measurement in that the determined pressure is independent of the gas species. At lower pressures, gauges tend to rely on measuring a particular physical property of the gas, and for this reason must generally be

calibrated to give correct measurements for the gas of interest. In this category, transport phenomena gauges measure gaseous drag on a moving body or exploit the thermal conductivity of the gas, while ionization gauges ionize the gas and measure the total ion current generated. The operating principles of some of the most common types of pressure gauge are outlined below.

1. U-tube manometer
   Range: 1 mbar to atmospheric pressure
   Type: mechanical
   This gauge consists of a U tube filled with mercury, silicon oil or some other non-volatile liquid. One end of the tube provides a reference pressure p_{ref}, and is either open to atmospheric pressure or sealed and evacuated to very low pressure. The other end of the U-tube is exposed to the system pressure to be measured, p_{sys}. The gas at each end of the tube applies a force to the liquid column through collisions with the liquid surface. If the pressures at each end of the tube are unequal then these forces are unbalanced, and the liquid will move along the tube until the forces are balanced. At the equilibrium point, the liquid in its new position exerts a force per unit area $p = \rho g \Delta h$, where ρ is the density of the liquid, g is the acceleration due to gravity, and Δh is the height difference between the two arms of the U- tube. Since this quantity must be equal to the original pressure differential between the two arms of the U-tube, the system pressure is therefore $p_{sys} = p_{ref} + \rho g \Delta h$.
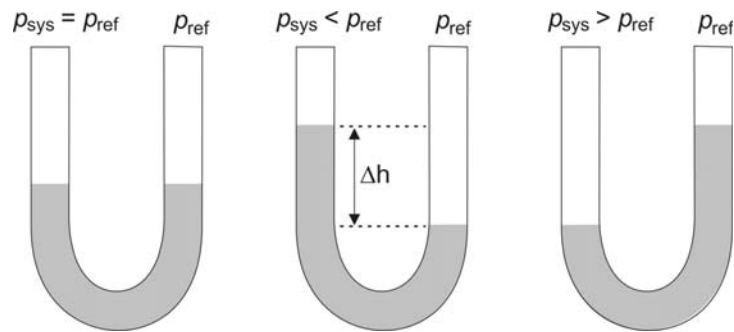

2. Bourdon gauge
   Range: 1 mbar – high pressure (at least tens of bar)
   Type: mechanical
   A Bourdon gauge works on essentially the same principle as a party blower. As shown in the diagram below, the gauge head contains a 'C' shaped fine-walled hollow metal tube (called a Bourdon tube). When pressurised, the cross section of the tube changes and the tube flexes and attempts to straighten. The tube is connected by a gearing system that transforms the flexion of the tube into rotation of a pointer, which indicates the pressure on a scale.
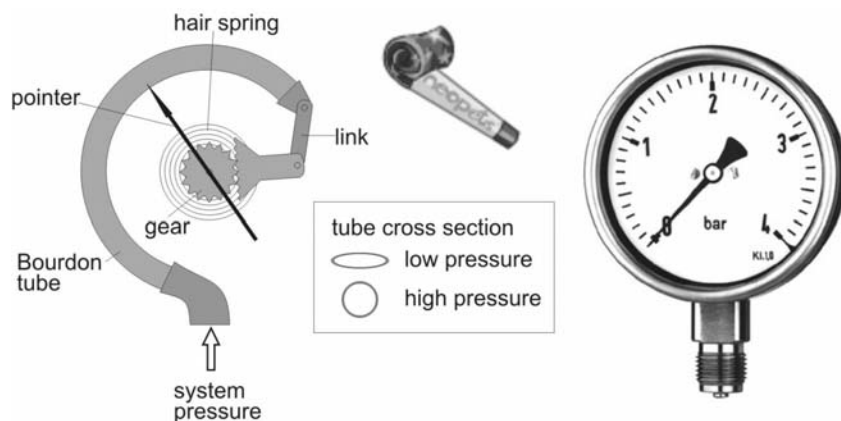
3. Capacitance manometer
    Range: $10^{-6} – 10^5$ mbar
    Type: mechanical
    A capacitance manometer (also known as a baratron) contains a thin metal diaphragm that is deflected when the pressure changes. The deflection is sensed electronically via a change in capacitance between the diaphragm and one or more fixed electrodes. One side of the diaphragm is maintained at a reference pressure, and the measured capacitance therefore allows an absolute pressure to be determined. The above diagram and some of those following were taken from http://www.lesker.com/newweb/Gauges/gauges_technicalnotes_1.cfm.
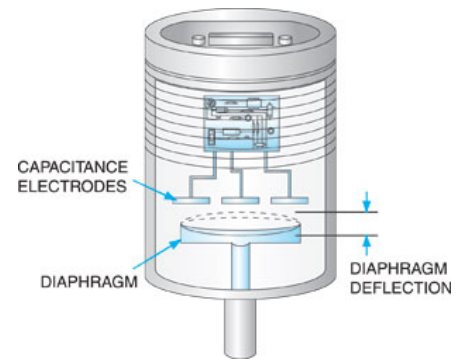
4. Pirani gauge
   *Range: $1000 – 10^{-4}$ mbar*
    Type: transport
    A Pirani gauge contains a metal wire that is heated by an electrical current. At the same time, collisions with the surrounding gas carry heat away from the wire and cool it, with the net effect being that the wire temperature settles at some equilibrium value. If the pressure is lowered, heat is carried away less effectively and the temperature of the wire increases, while an increase in pressure leads to more effective cooling and a decrease in the wire temperature. The temperature of the wire may therefore be used to measure the pressure. In practice this is achieved by monitoring the electrical resistance of the wire, which is temperature-dependent.

5. Thermocouple gauge
    Range: $1000-10^{-4}$ mbar
   *Type: transport*
    Thermocouple gauges work in a very similar way to Pirani gauges, except that a thermocouple is used to measure the temperature of the wire directly, rather than inferring the temperature from a measurement of the resistance.
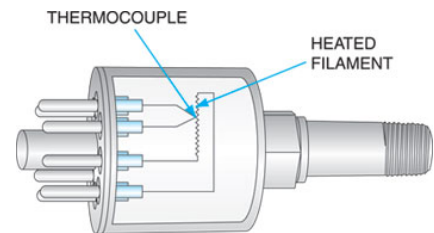
6. Hot cathode ionization gauge (Bayard-Alpert gauge)
    Range: $10^{-3} – 10^{-10}$ mbar
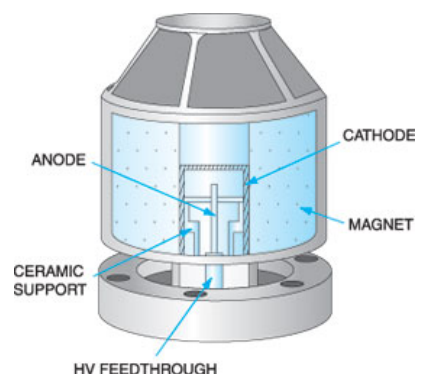   *Type: ionization*
    A hot cathode gauge consists of a heated filament that emits electrons, an acceleration grid, and a thin wire detector. Electrons emitted from the filament are accelerated towards the grid, and ionise gas molecules along the way. The ions are collected at the detection wire, and the measured ion current is proportional to the gas pressure. This type of ionization gauge has the advantage that there is a linear dependence of the ion current on the gas pressure. Like any ionization gauge, correction factors need to be applied for different gases to account for differences in electron-impact ionization probability.
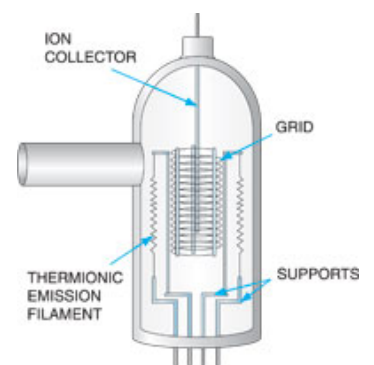
7. Cold cathode ionization gauge (Penning gauge)
    Range: $10^{-2} – 10^{-7}$ mbar
    Type: ionization
    A cold cathode gauge (see figure on right) works on a similar principle to a hot cathode gauge, but the mechanism of ionization is somewhat different. There is no filament to produce electrons, simply a detection rod (the anode) and a

cylindrical cathode, to which a high voltage (~4kV) is applied. Ionization is initiated randomly by a cosmic ray or some other ionizing particle entering the gauge head (this occurs more frequently than you might think!). The electrons formed are accelerated towards the anode. A magnetic field causes them to follow spiral trajectories, increasing the path length through the gas, and therefore the chance of ionizing collisions. The ions are accelerated towards the cathode, where they are detected. More free electrons are emitted as the ions bombard the cathode, further increasing the signal. Eventually a steady state is reached, with the ion current being related to the background gas pressure. The relationship is not a linear one as in the case of a hot cathode gauge, and the pressure reading is only accurate to within around a factor of two. However, in its favour, the Penning gauge is more damage resistant than a hot cathode gauge.
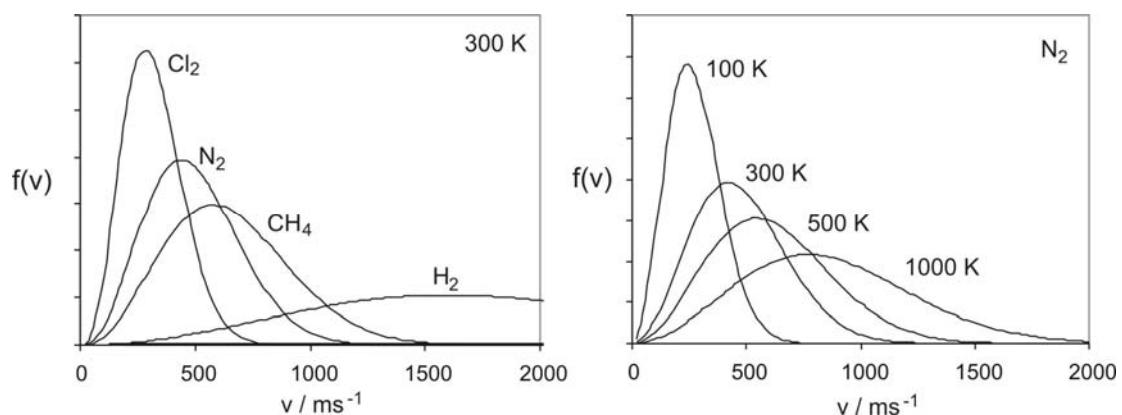
Temperature

The temperature of a gas is a measure of the amount of kinetic energy the gas particles possess, and therefore reflects their velocity distribution. If we followed the velocity of any single particle within a gas, we would see it changing rapidly due to collisions with other particles and with the walls of the container. However, since energy is conserved, these collisions only lead to exchange of energy between the particles, and the total number of particles with a given velocity remains constant i.e. at a given temperature, the velocity distribution of the gas particles is conserved.

Note that temperature is a direct result of the motion of atoms and molecules. In a solid this motion is almost exclusively vibrational; in a gas it is predominantly translational. Whatever the type of motion, an important consequence is that the concept of temperature only has any meaning in the presence of matter. It is impossible to define the temperature of a perfect vacuum, for example. In addition, temperature is only really a meaningful concept for systems at thermal equilibrium. The distribution of molecular speeds $f(v)$ in an ideal gas at thermal equlibrium is given by the following expression, known as the Maxwell-Boltzmann distribution (this will be derived in Section 6).

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right) \quad \text{Maxwell-Boltzmann distribution} \quad (3.2)$$

The distribution depends on the ratio m/T, where m is the mass of the gas particle and T is the temperature. The plots below show the Maxwell Boltzmann speed distributions for a number of different gases at two different temperatures.

As we can see, average molecular speeds for common gases at room temperature (300 K) are generally a few hundred metres per second. For example, N_2 has an average speed of around 500 ms^{-1}, rising to around 850 ms^{-1} at 1000 K. A light molecule such as H_2 has a much higher mean speed of around 1800 ms^{-1} at room temperature.

We can make two observations:

1. Increasing the temperature broadens the distribution and shifts the peak to higher velocities. This means that there are more 'fast' particles at higher temperatures, but there will still be many 'slow' ones as well.

2. Decreasing the mass of the gas particles has the same effect as increasing the temperature i.e. heavier particles have a slower, narrower distribution of speeds than lighter particles.

A good java applet demonstration of these ideas may be found on the chemistry website for Oklahoma State University: http://intro.chem.okstate.edu/1314F00/Laboratory/GLP.htm

We will consider some further consequences of the Maxwell-Boltzmann distribution when we look at collisions in the next lecture. Now we will consider the measurement of temperature.

Based on our current definition, one way to measure the temperature of a gas would be to measure the velocities of each particle and then to find the appropriate value of T in the above expression to match the measured distribution. This is clearly impractical, due both to the extremely high speeds of the gas particles and the difficulties associated with tracking any given particle amongst a sea of identical particles. Instead, temperature measurements generally rely on the process of thermal equilibration.

Thermal equilibrium and temperature measurements

If two objects at different temperatures are placed in contact, heat will flow from the hotter object to the cooler object until their temperatures equalise. When the two temperatures are equal, we say the objects are in *thermal equilibrium.* The concept of thermal equilibrium provides the basis for the 'zeroth law' of thermodynamics.

> *If A is in thermal equilibrium with B and B is in thermal equilibrium with C, then A is also in thermal equilibrium with C.*

This provides the basis for a rather formal definition of temperature as being 'that property which is shared by objects in thermal equilibrium with each other'. The zeroth law may seem very obvious, but it is an important principle when it comes to measuring the temperature of a system. In general, it usually won't be practical to place two arbitrary systems in thermal contact to find out if they are in thermal equilibrium and therefore have the same temperature. However, the zeroth law means that we can use the properties of some reference system to establish a temperature scale, calibrate a measuring device to this reference system, and then use the device to measure the temperature of other systems. An example of such a device is a mercury thermometer. The reference system is a fixed quantity of mercury, and the physical property used to establish the temperature scale is the volume occupied by the mercury as a function of temperature. To make a temperature measurement, the mercury is allowed to come into thermal equilibrium with the system we are making the measurement on, and the volume occupied by the mercury once equlibrium has been established may be converted to a temperature on our previously-established scale.

Standard mercury or alcohol thermometers therefore rely on the physical property of thermal expansion of a fluid for temperature measurement. However, many other properties may also be used to measure temperature. Some of these include:

Electrical resistance – the resistance of an electrical conductor or semiconductor changes with temperature. Devices based on metallic conductors are usually known as 'resistance temperature devices', or RTDs, and rely on the more-or-less linear rise in resistance of a metal with increasing temperature. A second type of device is the thermistor, which is based on changes in resistance in

a ceramic semiconductor.   Unlike metallic conductors, the resistance of these devices drops non-linearly as the temperature is increased.

Thermoelectric effect – When a metal is subjected to a thermal gradient, a potential difference is generated. This effect is known as the thermoelectric (or Seebeck) effect, and forms the basis for a widely used class of temperature measurement devices known as thermocouples.

Infrared emission – all substances emit black body radiation with a wavelength or frequency distribution that reflects their temperature. Infrared temperature measurement devices measure emission in the IR region of the spectrum in order to infer the temperature of a substance or object.

Thermal expansion of solids – bimetallic temperature measurement devices consist of two strips of different metals, bonded together. The different thermal expansion coefficients of the metals mean that one side of the bonded strip will expand more than the other on heating, causing the strip to bend. The degree of bending provides a measure of the temperature.

Changes of state – thermometers based on materials that undergo a change of state with temperature are becoming increasingly widespread. For example, liquid crystal thermometers undergo a reversible colour change with changes in temperature.   Other materials undergo irreversible changes, which may be useful in situations where all we need to know is whether a certain temperature has been exceeded (e.g. packaging of temperature sensitive goods).

4. Experimental observations – the gas laws

Now that we have considered the physical properties of a gas in some detail, we will move on to investigating relationships between them.   The figure on the right illustrates the observed relationship between the volume and pressure of a gas at two different temperatures.
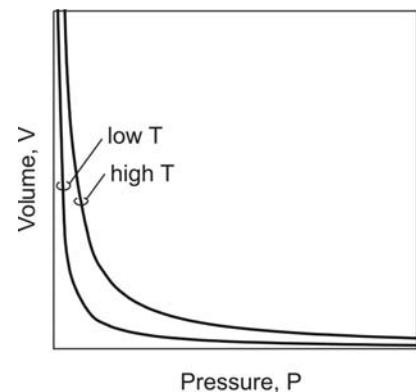

The relationship between pressure and volume

Initially, we will focus on just one of the curves in order to look at the relationship between pressure and volume. We see that as we increase the pressure from low values, the volume first drops precipitously, and then at a much slower rate, before more or less leveling out to a constant value. In fact, we find that pressure is inversely proportional to volume, and the curves follow the equation

$$pV = \text{constant} \qquad\qquad \text{Boyle's law} \qquad\qquad (4.1)$$

This relationship, known as Boyle's law, suggests that it becomes increasingly more difficult to compress a gas as we move to higher pressures.   It is fairly straightforward to explain this observation using our understanding of the molecular basis of pressure.   Consider the experimental setup shown in the figure below, in which a gas is compressed by depressing a

plunger that forms the 'lid' of the container when the plunger is at its highest position (left hand side of the figure), the volume occupied by the gas is large and the pressure is low. The low pressure means that there are relatively few collisions of the gas with the inside surface of the plunger, and the force opposing depression of the plunger is correspondingly low. Under these conditions it is therefore very easy to compress the gas. Once the plunger has already been depressed some way (right hand figure), the gas occupies a much smaller volume, and there are many more collisions with the inside surface of the plunger (i.e. a higher pressure).   These
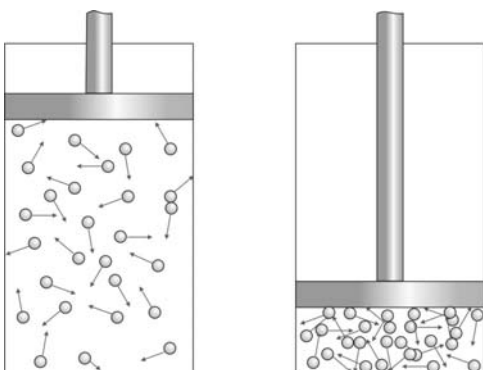
collisions provide a large force opposing further depression of the plunger, and it becomes much more difficult to reduce the volume of the gas.

The effect of temperature on pressure and volume

From the plot above, we see that for a fixed volume, the pressure increases with temperature. In fact, this is a direct proportionality:

$$P \propto T \quad \text{(at constant volume)} \tag{4.2}$$

Similarly, we find that at a fixed pressure, the volume is linearly dependent on temperature.

$$V \propto T \quad \text{(at constant pressure)} \tag{4.3}$$

This second relationship is known as Charles's law (or sometimes Gay-Lussac's law). It is often written in the slightly different (but equivalent) form

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad \text{Charles' law} \tag{4.4}$$

The first two equations above may be combined to give the result

$$pV \propto T \tag{4.5}$$

These observations are again very straightforward to explain using our molecular understanding of gases. The primary effect of increasing the temperature of the gas is to increase the speeds of the particles. As a result, there will be more collisions with the walls of the container (or the inside surface of the plunger in our example above), and the collisions will also be of higher energy. For a fixed volume of gas, these factors combine to give an increase in pressure. On the other hand, if the experiment is to be carried out at constant pressure, we require that the total force exerted upwards on the plunger through collisions remains constant. Since the individual collisions are more energetic at higher temperatures, this may only be achieved by reducing the number of collisions, which requires a reduction in the density of the gas and therefore an increase in its volume.

The effect of the amount of gas, n

It follows fairly intuitively from the arguments above that both pressure and volume will also be proportional to the number of gas molecules in the sample. i.e.

$$pV \propto n \tag{4.6}$$

This is known as Avogadro's principle.

Equation of state for an ideal gas

We can combine all of the above results into a single expression, which turns out to be the equation of state for an ideal gas (and an approximate equation of state for real gases).

$$pV = nRT \qquad \text{Ideal gas law} \tag{4.7}$$

The constant of proportionality, R, is called the gas constant, and takes the value 8.314 J K^{-1} mol^{-1}. Note that R is related to Boltzmann's constant, k_B, by $R = N_A k_B$, where N_A is Avogadro's number.

This equation generally provides a good description of gases at relatively low pressures and moderate to high temperatures, which are the conditions under which the original experiments

described above were carried out. To understand the reasons for this, and also the reasons that the equation breaks down at high pressures and low temperatures, we need to consider the differences between an 'ideal' gas and a real gas.

5. Ideal gases and real gases

The ideal gas model

The ideal gas model is an approximate model of gases that is often used to simplify calculations on real gases. An ideal gas has the following properties:

1.   There are no intermolecular forces between the gas particles.

2.   The volume occupied by the particles is negligible compared to the volume of the container they occupy.

3.   The only interactions between the particles and with the container walls are perfectly elastic collisions.

Note that an elastic collision is one in which the total kinetic energy is conserved (i.e. no energy is transferred from translation into rotation or vibration, and no chemical reaction occurs). Of course, in a real gas, the atoms or molecules have a finite size, and at close range they interact with each other through a variety of intermolecular forces, including dipole-dipole interactions, dipole-induced dipole interactions, and van der Waal's (induced dipole – induced dipole) interactions. When applied to real gases, the ideal gas model breaks down when molecular size effects or intermolecular forces become important. This occurs under conditions of high pressure, when the molecules are forced close together and therefore interact strongly, and at low temperatures, when the molecules are moving slowly and intermolecular forces have a long time to act during a collision. The pressure at which the ideal gas model starts to break down will depend on the nature and strength of the intermolecular forces between the gas particles, and therefore on their identity. The ideal gas model becomes more and more exact as the pressure is lowered, since at very low pressures the gas particles are widely spaced apart and interact very little with each other.

The compression factor

The deviations of a real gas from ideal gas behaviour may be quantified by a parameter called the *compression factor,* usually given the symbol *Z*. At a given pressure and temperature, attractive and repulsive intermolecular forces between gas particles mean that the molar volume is likely to be smaller or larger than for an ideal gas under the same conditions. The compression factor is simply the ratio of the molar volume V_m of the gas to the molar volume V_m^o of an ideal gas at the same pressure and temperature.

$$Z = \frac{V_m}{V_m^o}$$

The value of Z provides information on the dominant types of intermolecular forces acting in a gas.

      Z = 1   No intermolecular forces, ideal gas behaviour
      Z < 1   Attractive forces dominate, gas occupies a smaller volume than an ideal gas.
      Z > 1   Repulsive forces dominate, gas occupies a larger volume than an ideal gas.

All gases approach Z=1 at very low pressures, when the spacing between particles is large on average. To understand the behaviour at higher pressures we need to consider a typical intermolecular potential, *V*(*r*), (see figure below) which describes the energy of interaction between two molecules as a function of their separation. We can divide the potential into three regions or zones, as illustrated in the diagram, and consider the value of *Z* in each region.

Region I – large separations

At large separations the interaction potential is effectively zero and Z = 1. When the molecules are widely separated we therefore expect the gas to behave ideally, and this is indeed the case, with Z tending towards unity for all gases at sufficiently low pressures.


Region II – small separations

As the molecules approach each other, they experience an attractive interaction (i.e. the system is able to decrease its energy by the molecules moving closer together). This draws the molecules in the gas closer together than they would be in an ideal gas, reducing the molar volume such that Z < 1.

Region III – very small separations

At very small separations, the electron clouds on the molecules start to overlap, giving rise to a strong repulsive force (bringing the molecules closer together now increases their potential energy). Because they are repelling each other, the molecules now take up a larger volume than they would in an ideal gas, and Z > 1.
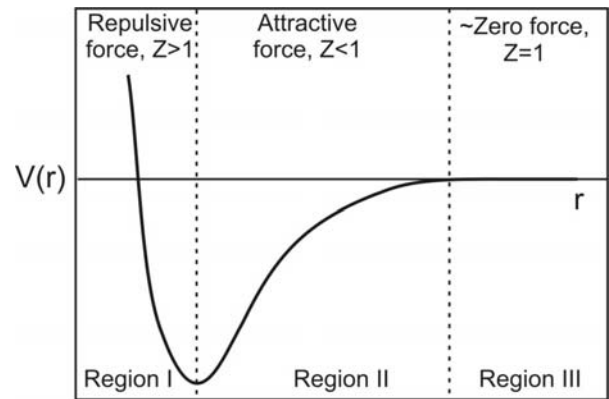
The behaviour of *Z* with pressure for a few common gases at a temperature of 273 K (0 °C) is illustrated below.
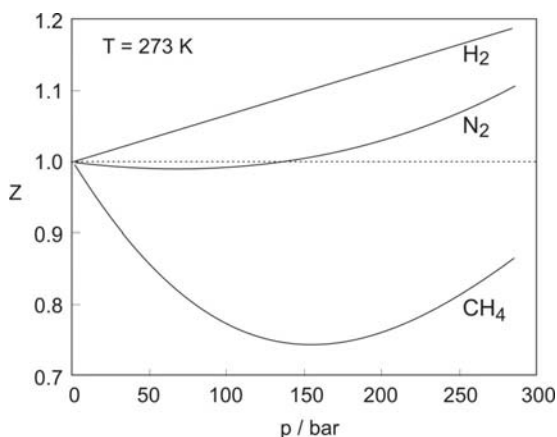
The compression factor also depends on temperature. The reasons for this are twofold, but both stem from the increased speed of the molecules. Firstly, at higher speeds there is less time during a collision for the attractive part of the potential to act and the effect of the attractive intermolecular forces is therefore smaller (see left panel on diagram below). Secondly, the higher energy of the collisions means that the particles penetrate further into the repulsive part of the potential during each collision, so the repulsive interactions become more dominant (see centre panel below). The temperature of the gas therefore changes the balance between the contributions of attractive and repulsive interactions to the compression factor. The resulting pressure-dependent compression factor for N_2 at three different temperatures is shown below on the right.
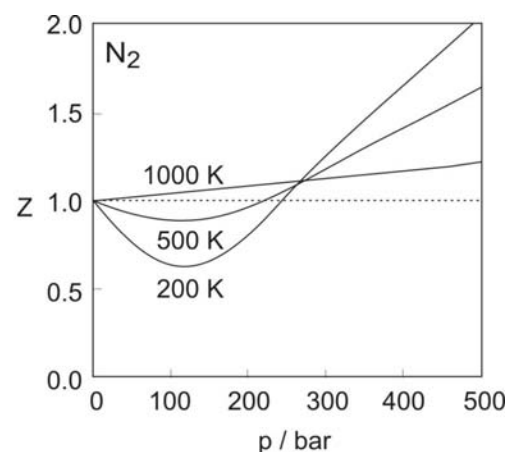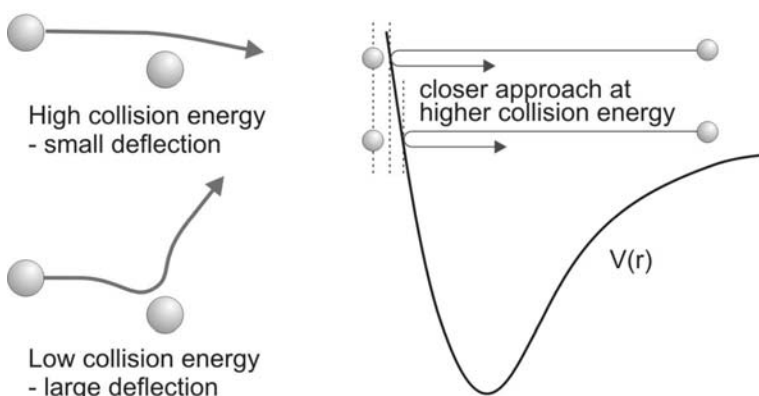
Finally, we should consider the rate of change of Z with pressure. An ideal gas has $Z = 1$ and $dZ/dp = 0$ (i.e. the slope of a plot of Z against p is zero) at all pressures. For all real gases, Z tends towards unity at low pressures. However, dZ/dp only tends towards zero in this pressure range at a single temperature called the *Boyle temperature, T_B*. At the Boyle temperature, the attractive and repulsive interactions exactly balance each other and the real gas behaves ideally over a certain range of pressures.

Equations of state for real (non-ideal) gases

There are a number of ways in which the ideal gas equation (Equation 1.6.8) may be modified to take account of the intermolecular forces present in a real gas. One way is to treat the ideal gas law as the first term in an expansion of the form:

$$pV = RT\,(1 + B'p + C'p^2 + ...) \tag{5.1}$$

This is known as a *virial expansion*, or sometimes as the *virial equation of state*, and the coefficients B', C' etc are called *virial coefficients*. Often, a more convenient form for the virial expansion is:

$$pV = RT\left(1 + \frac{B}{V} + \frac{C}{V^2} + ...\right) \tag{5.2}$$

In many applications, only the first correction term (the term with coefficient B or B') is included. Note that the Boyle temperature mentioned above is the temperature at which the first virial coefficient $B = 0$.

Another widely used equation for treating real gases is the van der Waal's equation.

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \tag{5.3}$$

where a and b are temperature-independent constants called the van der Waal's coefficients. Each gas has its own characteristic van der Waal's coefficients. This equation is often expressed in terms of molar volumes V_m.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{5.4}$$

6. The kinetic theory of gases

Now that most of the basic concepts underlying the properties of gases have been covered, we are ready to move on to a more quantitative description. The ideal gas model, which represents a simplified approximate version of a real gas, has already been introduced. We will find in the following sections that we can use this model as the basis for the *kinetic theory of gases*. The name comes from the fact that within kinetic theory, it is assumed that the only contributions to the energy of a gas arise from the kinetic energies of the gas particles (this is implicit in the assumptions of the ideal gas model listed at the start of Section 5).

Kinetic theory is a powerful model that allows us to relate macroscopic measurable quantities to motions on the molecular scale. In the following sections, we will use it to calculate 'microscopic' quantities such as average particle velocities, collision rates and the distance travelled between collisions, and to investigate macroscopic properties such as pressure and transport phenomena (e.g. diffusion rates and thermal conductivity).

7. Collisions with the container walls - determining pressure from molecular speeds

As described in Section 3, the measured pressure of a gas arises from collisions of the gas particles with the walls of the container. By considering these collisions more carefully, we can use kinetic theory to relate the pressure directly to the average speed of the gas particles. Firstly, we will determine the momentum transferred to the container walls in a single collision. The figure below shows a particle of mass m and velocity $\boldsymbol{v}$ colliding with a wall of area A. Before the collision, the particle has velocity v_x and momentum mv_x along the x direction. After the collision, the particle has momentum $-mv_x$ along the x direction (note that the components of momentum along y and z remain unchanged). Since momentum must be conserved during the collision, and the momentum of the particle has changed by $2mv_x$, the total momentum imparted to the wall must also be $2mv_x$.
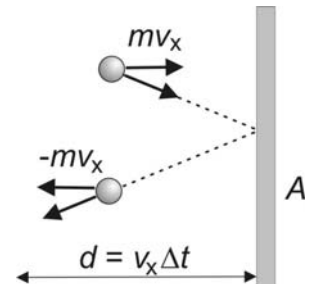
The next step is to determine the total number of collisions with the wall in a given time interval Δt. During this time interval, all particles within a distance $d = v_x\Delta t$ of the wall (and travelling towards it) will collide with the wall. Since the area of the wall is A, this means that all particles within a volume $Av_x\Delta t$ will undergo a collision. We now need to work out how many particles will be within this volume and travelling towards the wall. The number density of the molecules (i.e the number of molecules per unit volume) is

$$\text{number density} = \frac{N}{V} = \frac{nN_A}{V} \tag{7.1}$$

where N is the number of molecules and n the number of moles in the container of volume V. The number of molecules within our volume of interest, $Av_x\Delta t$, is therefore just the number density multiplied by this volume. i.e.

$$\text{number of molecules} = \frac{nN_A}{V} Av_x\Delta t \tag{7.2}$$

Since the random velocities of the particles mean that on average half of the molecules in the container will be travelling towards the wall and half away from it, the number of molecules within our volume travelling towards the wall is half of the above value. The total momentum imparted to the wall is now just the momentum change per collision multiplied by the total number of collisions.

$$\Delta p_x = (2mv_x) \left(\frac{1}{2} \frac{nN_A}{V} Av_x\Delta t \right) = \frac{nMAv_x^2\Delta t}{V} \tag{7.3}$$

where we have used $M = mN_A$.

Pressure is defined as the force per unit area, so we need to convert the above momentum into a force in order to calculate the pressure. We can do this using Newton's second law of motion.

$$F_x = ma_x = m\frac{dv_x}{dt} = \frac{dp_x}{dt} \tag{7.4}$$

Applying this to Equation (6.3), we obtain

$$F_x = \frac{dp_x}{dt} = \frac{\Delta p_x}{\Delta t} = \frac{nMAv_x^2}{V} \tag{7.5}$$

The pressure is therefore

$$p = \frac{F_x}{A} = \frac{nMv_x^2}{V} \tag{7.6}$$

Finally, there is a small amount of 'tidying up' to carry out on this expression. Since we have based our arguments on a particle with a single velocity v_x, and in reality there is a distribution of velocities in the gas, we should replace v_x^2 with $<v_x^2>$, the average of this quantity over the distribution. We can simplify things still further by recognising that the random motion of the particles means that the average speed along the x direction is the same as along y and z. This allows us to define a root mean square speed

$$v_{rms} = [<v_x^2> + <v_y^2> + <v_z^2>]^{1/2} = [3<v_x^2>]^{1/2} \tag{7.7}$$

such that $<v_x^2> = \frac{1}{3}v_{rms}^2$

Our final expression for the pressure is therefore

$$p = \frac{1}{3}\frac{nMv_{rms}^2}{V} \qquad \text{or} \qquad pV = \frac{1}{3}nMv_{rms}^2 \tag{7.8}$$

Since the average speed of the molecules is constant at constant temperature, note that by our simple treatment of collisions with a surface, we have in fact just derived Boyle's law.

$$pV = \text{constant} \quad \text{(at constant temperature)} \tag{7.9}$$

From this point, it is fairly straightforward to go one step further and derive the ideal gas law. Recall that the equipartition theorem states that each translational degree of freedom possessed by a molecule is accompanied by a ½ kT contribution to its internal energy. Each molecule in our sample has three translational degrees of freedom. Also, because in the kinetic model, the only contribution to the internal energy of the system is the kinetic energy ½ mv_{rms}^2 of the molecules, we therefore have:

$$\frac{3}{2}k_B T = \frac{1}{2}mv_{rms}^2 \tag{7.10}$$

Multiplying both sides through by Avogadro's number, N_A, and rearranging slightly gives

$$RT = \frac{1}{3}Mv_{rms}^2 \tag{7.11}$$

Finally, substituting this result into equation (7.8) yields the ideal gas law.

$$pV = nRT \tag{7.12}$$

Our simple kinetic model of gases can therefore explain all of the experimental observations described in Section 4.

8. The Maxwell Boltzmann distribution revisited

In Section 3 we introduced the Maxwell Boltzmann distribution, describing the velocity distribution of gas molecules at thermal equilibrium. There are various ways in which this distribution may be derived. In the following version much of the hard work is done by means of fairly straightforward symmetry arguments.

We will start by breaking the velocity **v** down into its components v_x, v_y and v_z and considering the probability $p(v_x)dv_x$ that a particle has a velocity component v_x in a range dv_x i.e. lies between v_x and v_x+dv_x. Since each velocity component may be treated independently, according to probability theory the total probability of finding a particle with components v_x, v_y, v_z in the range dv_x, dv_y, dv_z is just the product of the probabilities for each component.

$$P(v_x,v_y,v_z)\, dv_x dv_y dv_z = p(v_x)dv_x\, p(v_y)dv_y\, p(v_z)dv_z \tag{8.1}$$

If we stop and think for a moment, we can reason that since the directions the particles are travelling in are completely random and that all directions within the gas are equivalent, the distribution function $P(v_x, v_y, v_z)$ can actually only depend on the total speed v of the particle rather than on the individual velocity components. To express v in terms of the components we use the fact that $v^2 = v_x^2 + v_y^2 + v_z^2$. The probability distribution function[1] may now be written as $P(v_x^2 + v_y^2 + v_z^2)$, and we have

$$P(v_x^2 + v_y^2 + v_z^2)\, dv_x dv_y dv_z = p(v_x)\, p(v_y)\, p(v_z)\, dv_x dv_y dv_z \qquad (8.2)$$

and therefore

$$P(v_x^2 + v_y^2 + v_z^2) = p(v_x)\, p(v_y)\, p(v_z) \qquad (8.3)$$

The only type of function that satisfies a relationship of this kind is an exponential (using the fact that $e^{x+y+z} = e^x e^y e^z$) so we can see immediately that the functions $p(v_x)$, $p(v_y)$, $p(v_z)$ on the right must in fact be exponential functions of v_x^2, v_y^2 and v_z^2. It is fairly easy to show that a suitable solution is:

$$p(v_x) = A \exp(-B v_x^2) \qquad (8.4)$$

with analagous expressions for $p(v_y)$ and $p(v_z)$. The argument in the exponential is negative because energy constraints mean that for our model to make physical sense, the probability of finding a particle must decrease as we go to higher particle speeds. Determining the two constants is fairly straightforward. Since $p(v_x)$ is a probability distribution, it must be normalised to unity. i.e.

$$1 = \int_{-\infty}^{\infty} p(v_x) dv_x = A \int_{-\infty}^{\infty} \exp(-B v_x^2) dv_x = A \left(\frac{\pi}{B}\right)^{1/2} \qquad (8.5)$$

Therefore, $A = (B/\pi)^{1/2}$. We can now determine B by using our distribution to calculate a property that we already know. From Equation (7.7 and 7.11), we have

$$\langle v_x^2 \rangle = \frac{1}{3} v_{rms}^2 = \frac{k_B T}{m} \qquad (8.6)$$

We can also calculate $\langle v_x^2 \rangle$ using our probability distribution in Equation (8.14). The average value of a property x that can take any value in a continuous range, and has a probability $p(x)$ of taking a particular value, is given by $\langle x \rangle = \int x\, p(x)\, dx$. We therefore have

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2\, p(v_x)\, dv_x = \left(\frac{B}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} v_x^2 \exp(-B v_x^2) dv_x \qquad (8.7)$$

As in (8.5), this is a standard integral and has the value $\frac{1}{2}\left(\frac{\pi}{B^3}\right)^{1/2}$, giving $\langle v_x^2 \rangle = \frac{1}{2B}$. Therefore, from (8.6), we have $B = \frac{m}{2 k_B T}$, and our probability distribution function is

$$p(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp(-m v_x^2 / 2 k_B T) \qquad (8.8)$$

Our final step is to use this result to determine the distribution of molecular speeds (rather than just the distribution of a single velocity component). From equation (8.1), this is simply

$$P(v_x, v_y, v_z)\, dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp(-m v^2 / 2 k_B T)\, dv_x dv_y dv_z \qquad (8.9)$$

---

[1] Note that $P(v_x^2 + v_y^2 + v_z^2)$ is the probability distribution function. To obtain a probability of the particle having a particular set of velocity components, it must be multiplied by the volume element $dv_x dv_y dv_z$.

The above expression gives the probability of the speed distribution having components v_x, v_y, v_z, whereas what we would really like to know is the probability $P(v)dv$ that the molecular speed lies in the range v to $v+dv$. This is simply the sum of the probabilities that it lies in any of the volume elements $dv_x dv_y dv_z$ within the spherical shell bounded by the two radii v and $v+dv$ (i.e. a shell of radius v and thickness dv). The appropriate volume element for the distribution is therefore the volume of this shell, which is $4\pi v^2 dv$. We substitute this for the volume element $dv_x dv_y dv_z$ in the above expression to give the final form for the Maxwell-Boltzmann distribution of molecular speeds.

$$P(v)dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp(-mv^2/2k_B T)\, dv \qquad (8.10)$$

Mean speed, most probable speed and root-mean-square speed of the particles in a gas

We can use the Maxwell Boltzmann distribution to determine the mean speed and the most probable speed of the particles in the gas. Since the probability distribution is normalised, the mean speed is determined from the following integral:

$$<v> = \int_0^\infty v\, P(v)dv \qquad (8.11)$$

When we substitute for P(v) and carry out the integral, we obtain

$$<v> = \left(\frac{8k_B T}{\pi m}\right)^{1/2} \qquad \textit{Mean speed} \qquad (8.12)$$

With a little more work, this result may be generalised to give the mean relative speed between two particles of masses m_A and m_B.

$$<v_{rel}> = \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} \qquad \textit{Mean relative speed} \qquad (8.13)$$

where $\mu = m_A m_B/(m_A+m_B)$ is the reduced mass of the particles.

We can find the most probable speed by maximising the distribution in Equation (8.10) with respect to v (a good exercise if you fancy some practice at calculus), giving

$$v_{mp} = \left(\frac{2k_B T}{m}\right)^{1/2} \qquad \textit{Most probable speed} \qquad (8.14)$$

Another characteristic speed that is often used is the root-mean-square speed, which we met earlier. By rearranging Equation (8.6) we find that this is given by

$$v_{rms} = \left(\frac{3k_B T}{m}\right)^{1/2} \qquad \textit{RMS speed} \qquad (8.15)$$

9. Collisions

Collisions are one of the most fundamental processes in chemistry, and provide the mechanism by which both chemical reactions and energy transfer occur in a gas. The rate at which collisions occur determines the timescale of these events, and is therefore an important property for us to be able to calculate. The rate of collisions is usually expressed as a *collision frequency*, defined as the number of collisions a molecule undergoes per unit time. We will use kinetic theory to calculate collision frequencies for two cases: collisions with the container walls; and intermolecular collisions.

(i) Collisions with the container walls.

We have done much of the work required to calculate the frequency of collisions with the container walls in Section 7. There we showed that for a wall of area A, all molecules in a volume $Av_x\Delta t$ with positive velocities will collide with the wall in the time interval Δt. We can use our probability distribution $p(v_x)$ from Equation (8.8) to determine the average value $<V>$ of this volume

$$<V> = A\,\Delta t \int_0^\infty v_x\, p(v_x)\, dv_x = A\,\Delta t \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^\infty v_x \exp\left(\frac{-mv_x^2}{2k_B T}\right) dv_x = A\,\Delta t \left(\frac{k_B T}{2\pi m}\right)^{1/2} \qquad (9.1)$$

Multiplying the result by the number density of molecules, $\frac{N}{V} = \frac{p}{k_B T}$, yields the number of collisions occurring in the time interval Δt. For unit time and unit area ($A = 1$ m^2, $\Delta t = 1$ s), this yields a collision frequency

$$Z_{wall} = \frac{p}{k_B T}\left(\frac{k_B T}{2\pi m}\right)^{1/2} = \frac{p}{(2\pi m k_B T)^{1/2}} \qquad (9.2a)$$

Note that since $\left(\frac{k_B T}{2\pi m}\right)^{1/2}$ is equal to $<v>/4$, where $<v>$ is the mean speed defined in Equation (8.12), this is also sometimes written,

$$Z_{wall} = \frac{<v>N}{4V} \qquad (9.2b)$$

To give you an idea of the magnitude of this quantity, at 1 bar pressure and 298 K, N$_2$ molecules undergo about 2.9×10^{27} collisions with a 1 m^2 area of wall every second.

(i) Collisions with other molecules.

To determine the number of collisions a molecule undergoes with other molecules per unit time, we need to introduce the concept of the collision cross section, σ. This is defined as the cross sectional area that the centres of two particles must lie within if they are to collide. In the kinetic model, the particles act like hard spheres (there are no intermolecular forces) and a collision only occurs when the centres of two particles are separated by a distance equal to the particle diameter, d. This is shown in the figure below. Imagine that we have 'frozen' the motion of all of the particles apart from the darker coloured particle on the left. We can see that this particle will only collide with particles whose centres are within the cross sectional area $\sigma = \pi d^2$.

We can work out the collision frequency by looking at the figure in a little more detail. In a time interval Δt, the particle on the left will move a distance $<v>\Delta t$, represented by the length of the cylinder ($<v>$ is the average velocity of the particle). The number of collisions the particle undergoes in the time interval Δt will therefore be equal to the number density of particles in the gas, $N/V = p/k_B T$, multiplied by the volume $\sigma<v>\Delta t$ of the 'collision cylinder' the particle has sampled. We want to know the number of collisions per unit time, so we set $\Delta t = 1$ s. Also, since the particles are not really stationary, we need to replace $<v>$, the average speed of one molecule in the gas, by $<v_{rel}>$, the mean relative velocity of the gas particles. The collision frequency is therefore:
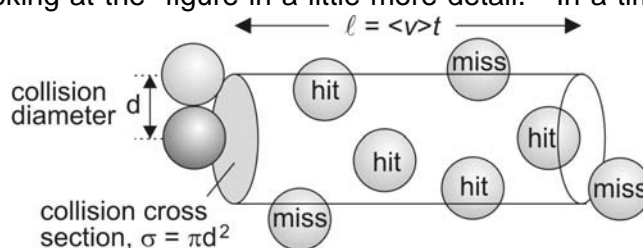
$$z = \sigma <v_{rel}>\frac{N}{V} = \sigma <v_{rel}>\frac{p}{k_B T} \qquad (9.3)$$

Note that the process of a single particle colliding with other particles in a gas is a first order rate process, and that the above expression is in fact simply a first order rate law of the form z = rate =

k[X]. In the gas phase it is more convenient to use number densities, N_X/V, or pressures, in place of concentrations [X]. In this case our rate law takes the form rate = K' (N_x/V), whith K' having a different value and units from k. Comparing this with Equation (9.3), we can identify the 'molecular scale' rate constant as the volume of the collision cylinder per unit time, $\sigma<v_{rel}>$.

The collision rate z that we have just calculated is the number of collisions made by a single molecule per second. Usually what we would like to know is the *total* collision frequency (also called the *collision density*) i.e. the total number of collisions occurring in the gas per unit volume per unit time. This is now a second-order rate process, with a rate equal to $K(N_x/V)^2$, or

$$Z_{XX} = \frac{1}{2} \sigma <v_{rel}> \left(\frac{N_X}{V}\right)^2 \tag{9.4}$$

The factor of ½ in this expression ensures that we avoid double counting of each collision (i.e. the collision of particle X with particle X′ is counted as the same collision as that of X′ with X, not as a separate one). Substituting for $<v_{rel}>$ from Equation (8.13) and using the fact that we can relate concentrations and number densities using [X]$N_A = N/V$, we can rewrite Equation (9.4) as

$$Z_{XX} = \sigma \left(\frac{4k_B T}{\pi m}\right)^{1/2} N_A^2 [X]^2 \tag{9.5}$$

Note that in the above we have used the fact that $\mu = \frac{m_Z m_Z}{m_Z + m_Z} = \frac{m_Z}{2}$ for the reduced mass.

Collision densities can be enormous. As an example, for N_2 gas under standard conditions, with a collision diameter of 0.28 nm, $Z_{XX} = 5 \times 10^{34}$ s^{-1} m^{-3}.

We can easily extend Equation (9.5) to cover collisions between different types of molecule, obtaining

$$Z_{XY} = \sigma \left(\frac{8k_B T}{\pi \mu}\right)^{1/2} N_A^2 [X][Y] \tag{9.6}$$

Note that in this case the collision cross section is still given by $\sigma = \pi d^2$, but the collision diameter is now given by $d = ½(d_X + d_Y)$, where d_X and d_Y are the diameters of X and Y.

Mean free path

The average distance a molecule travels between collisions is called the *mean free path*, usually given the symbol λ. The time between collisions is just the inverse of the collision frequency i.e. $1/z$. If the molecule is travelling at a mean speed $<v>$, then (since distance = velocity x time) the mean free path is

$$\lambda = \frac{<v>}{z} \tag{9.7}$$

At standard pressure and temperature, the mean free path is generally of the order of a few tens of nanometres. Since z is proportional to pressure, λ is inversely proportional to pressure e.g. doubling the pressure will halve the mean free path.

Effusion and gas leaks

A simple application of some of the concepts we have covered in this section on collisions is effusion, in which a gas at pressure p and temperature T escapes into a vacuum through a small hole of area a. Effusion occurs when the diameter of the hole is smaller than the mean free path in the gas, so that no collisions occur as the molecules pass through the hole. It is very simple to determine the rate of escape of the molecules, since this is just the rate at which they strike the hole.

$$\text{rate} = \frac{dN}{dt} = Z_{wall}\, a = \frac{pa}{(2\pi m k_B T)^{1/2}} \tag{9.8}$$

The fact that the rate of effusion is proportional to $1/m^{1/2}$ was originally observed experimentally and is known as *Graham's law of effusion*.

As the gas leaks out of the container, the pressure decreases, so the rate of effusion will be time dependent. The rate of change of pressure with time is

$$\frac{dp}{dt} = \frac{d(N k_B T/V)}{dt} = \frac{kT}{V}\frac{dN}{dt} \tag{9.10}$$

Substituting for $\frac{dN}{dt}$ and rearranging gives

$$\frac{dp}{p} = -\left(\frac{k_B T}{2\pi m}\right)^{1/2}\frac{a}{V}dt \tag{9.11}$$

which we can integrate to give

$$p = p_0 e^{-t/\tau} \qquad \text{with} \qquad \tau = \left(\frac{2\pi m}{k_B T}\right)^{1/2}\frac{V}{a} \tag{9.12}$$

Equation (9.12) has a number of uses. In log form, we have $\ln p = \ln p_0 - t/\tau$. Therefore, if we plot $\ln p$ inside our chamber against t, we can determine $\ln p_0$ and τ. A measurement of τ provides a simple way of determining the molecular mass, m, as long as the temperature and volume are constant. If we have a solid sample in our chamber, then the measurement of $\ln p_0$ yields the vapour pressure.

Molecular beams

State-of-the-art experiments in a number of areas of physical chemistry, including high resolution spectroscopy, reaction dynamics and surface science, employ molecular beams. Using beams of molecules provides a sample with a well defined velocity distribution, and allows directional properties of chemical processes to be studied. An example is a crossed molecular beam experiment, in which two molecular beams are crossed, usually at right angles, a chemical reaction occurs in the crossing region, and the speed and angular distribution of one or more of the products is measured. The measured scattering distribution can then be analysed to gain insight into the forces and energetics involved in the transition state region, and provides a direct probe of the fundamental physics underlying chemical reactivity.

Molecular beam scattering experiment

Product scattering distribution

Detailed understanding of reactive collision
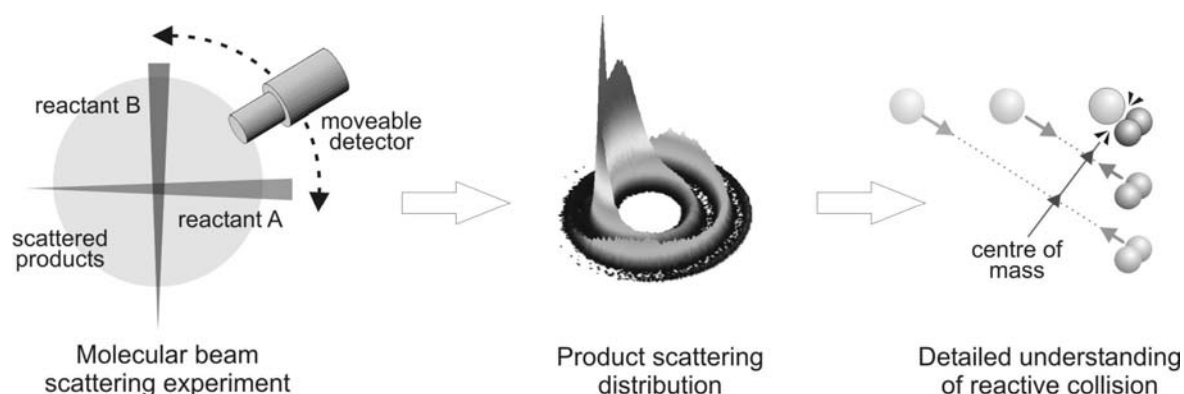
There are two types of molecular beam sources, known as effusive and supersonic sources, respectively. Both types of source work by allowing gas to escape from a 'high pressure' region through a small orifice into a vacuum. The difference between the two sources is that in an effusive source the diameter of the hole is smaller than the mean free path in the gas, and in a supersonic source it is larger. The orifice size is generally similar in the two types of source, but

the supersonic source operates at a much higher gas pressure, giving a much shorter mean free path than in the effusive source. The two types of beam have very different properties.

(i) Effusive sources
In an effusive beam, since molecules effectively 'wander' out of the hole whenever they 'collide' with it, the Maxwell-Boltzmann distribution of the molecular speeds in the source is more or less maintained in the molecular beam. The distribution is actually somewhat skewed towards higher velocities, since molecules with higher speeds undergo more collisions with the walls and are therefore more likely to exit the hole. The velocity components are conserved in the molecular beam, with the result that the beam has a broad $\cos^2\theta$ angular distribution, where θ is the angle between the molecular velocity and the beam axis (i.e. the direction normal to the wall of the chamber containing the hole). Effusive sources generally contain the gas at a low pressure, and are mainly only used to produce beams of metal atoms or other species that can only be prepared at low pressure in the gas phase. Usually the source is heated to high temperatures in order to obtain as high a vapour pressure as possible.

(ii) Supersonic sources
In supersonic sources, because the mean free path is much smaller than the diameter of the hole, many collisions occur as the molecules exit the hole and in the region immediately beyond it. Collisions that impart a velocity component along the beam axis will be most successful at allowing a molecule to escape this region, with the result that the molecules that end up in the beam are those for which the collisions have converted almost all of their random translational energy and internal (rotational and vibrational) energy into directed translational kinetic energy along the beam axis. The beam molecules therefore have almost no internal energy, occupying only very low rotational quantum states, and have a very narrow speed distribution. The angular distribution about the beam axis is also much narrower than for an effusive beam. Since the width of the molecular speed distribution determines the temperature of a gas, by this definition the molecules in a supersonic molecular beam are extremely cold. It is fairly standard to reach temperatures as low as 5 K by this very simple technique of expanding a gas through a small hole. The low temperatures in a molecular beam make them ideal for spectroscopic studies, since the small number of occupied quantum states often leads to a considerable simplification of the recorded spectrum relative to that of a room temperature sample.

10. Transport properties of gases

As the name suggests, a *transport property* of a substance describes its ability to transport matter or energy (or some other property) from one location to another. Examples include thermal conductivity (the transport of energy down a temperature gradient), electrical conductivity (transport of charge down a potential gradient), and diffusion (transport of matter down a concentration gradient). Viscosity is another transport property, since it describes the rate at which linear momentum is transported through a fluid. We can use kinetic theory to calculate several transport properties of gases. First however, we need to introduce the idea of a flux.

Flux

When dealing with transport properties, we are generally interested in the rate at which matter, energy, charge, or some other property is transported. We usually define this in terms of a *flux*, which is simply the amount of matter, energy, charge etc passing through a unit area per unit time. For example, *mass flux* is measured in units of kg m^{-2} s^{-1}, *energy flux* is measured in units of J m^{-2} s^{-1}, and so on. As described above, transport of some property generally occurs in response to a gradient in a related property, and the flux is generally proportional to the gradient. Note that both the flux and the gradient are vector properties. For example, if there is a concentration gradient in some direction z, there will be a component of mass flux in the same direction.

$$J_z(\text{matter}) \propto \frac{dn}{dz} \qquad\qquad (10.1)$$

Here, $n = N/V$ is the number density (don't get it confused with the number of moles of gas, also often given the symbol n). This proportionality of matter flux (more commonly known as *diffusion*) to the concentration gradient is often referred to as *Fick's first law of diffusion*. The constant of proportionality is called the *diffusion coefficient*, and is usually given the symbol D.

$$J_z(\text{matter}) = -D\frac{\mathrm{d}n}{\mathrm{d}z} \tag{10.2}$$

Note that we have given D a negative sign because matter diffuses down a concentration gradient from higher to lower concentration. i.e. if $\mathrm{d}n/\mathrm{d}z$ is negative (concentration decreasing in the positive z direction) then J_z will be positive (flow of matter in the positive z direction).

Similarly, if there is a temperature gradient along z, there will be a component of energy flux along z, which will determine the rate of thermal diffusion (or thermal conductivity). Again, since energy flows down a temperature gradient, the constant of proportionality, κ, takes a negative sign. κ is known as the coefficient of thermal conductivity.

$$J_z(\text{energy}) = -\kappa\frac{\mathrm{d}T}{\mathrm{d}z} \tag{10.3}$$

Viscosity is a slightly more subtle concept than diffusion or thermal conductivity. Formally, viscosity describes a fluid's resistance to deformation when subjected to a *shear stress*. When a force is applied to an object or material, the material exerts an opposing force (by Newton's third law). *Mechanical stress* is a measure of the internal distribution of force per unit area within the material that balances the external force. *Normal stress* is a stress state in which the stress is perpendicular to the face of the object, as would be the case when a compression force is applied normal to the surface. In *shear stress*, the stress is parallel to a face of the material. An example of shear stress would be the stress induced in a liquid trapped between two glass plates when the plates are moved across each other, as shown in the diagram below.
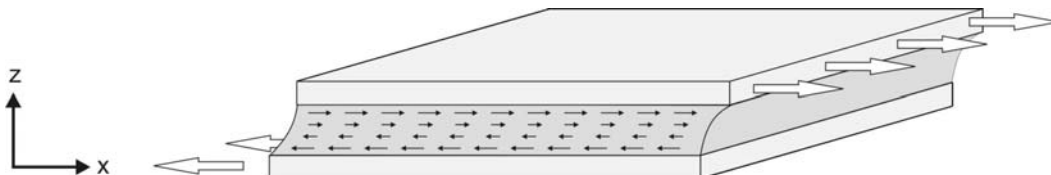
When we try to pour a fluid, we induce a shear stress as 'layers' of fluid try to move over each other. As stated above, viscosity is a measure of the deformation of the fluid under shear stress. Equivalently, we can think of viscosity as a measure of the internal friction within a fluid, and hence its internal resistance to flow. The viscosity of a fluid is generally observed as how 'thin' or 'thick' the fluid is, or in other words, how easy it is to pour. To give some examples, water has a fairly low viscosity and therefore flows easily, while treacle has a much higher viscosity and is much harder to pour.

In the figure above, we can see that the shear stress results in different velocity components of the fluid in the x direction as we move through the depth of the fluid (in the z direction). We therefore have a gradient in v_x along the z direction, and in analogy to diffusion and thermal conductivity above, this gives rise to a flux in v_x (or equivalently, in the momentum component p_x) along z.

$$J_z(\text{momentum along x}) = -\eta\frac{\mathrm{d}v_x}{\mathrm{d}z} \tag{10.4}$$

where η is the coefficient of viscosity (or more usually just 'the viscosity') of the fluid.

Now that we have defined the various transport phenomena, we will show how the kinetic theory of gases may be used to obtain values for the diffusion coefficient, D, the coefficient of thermal conductivity, k, and the coefficient of viscosity, η.

Diffusion

We can use kinetic theory both to show the molecular origins of Fick's first law of diffusion (that the flux of diffusing molecules is proportional to the concentration gradient), and also to determine a value for the diffusion coefficient, D. We will do this by considering the flux of molecules arriving from the left and from the right at an imaginary 'window' within a gas, as shown below. Within our gas, there is a concentration gradient from right to left (i.e. the concentration decreases from left to right).
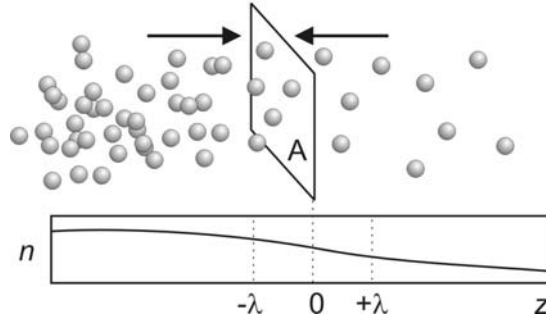
Since the motion of the gas molecules is randomised on each collision, the furthest a given molecule is able to travel in a particular direction is on average equal to a distance of one mean free path, λ. This means that to a first approximation we can assume that all of the particles arriving at the imaginary window over a time interval Δt have arrived there from a distance λ to the left or right, and the number densities of particles arriving from the left and right will therefore reflect the number densities at $z = -\lambda$ and $z = +\lambda$, respectively. If we approximate our concentration gradient to be linear between these two points (the two outer dotted lines on the graph above) with a slope equal to that at $z = 0$, i.e. $(dn/dz)_0$, then we can use the equation of a straight line to write these two number densities as

$$n(-\lambda) = n(0) - \lambda \left(\frac{dn}{dz}\right)_0 \quad \text{and} \quad n(+\lambda) = n(0) + \lambda \left(\frac{dn}{dz}\right)_0 \qquad (10.5)$$

From Equation (9.2b), which gives the number of collisions within a unit area per unit time, the fluxes from the left and right are therefore

$$J_L = \frac{<v>\, n(-\lambda)}{4} = \frac{<v>}{4}\left(n(0) - \lambda\left(\frac{dn}{dz}\right)_0\right) \qquad (10.6)$$

$$J_R = \frac{<v>\, n(+\lambda)}{4} = \frac{<v>}{4}\left(n(0) + \lambda\left(\frac{dn}{dz}\right)_0\right) \qquad (10.7)$$

The net flux in the z direction is therefore

$$J_z = J_L - J_R = -\frac{1}{2}\left(\frac{dn}{dz}\right)_0 \lambda <v> \qquad (10.8)$$

We have therefore shown that the flux is proportional to the concentration gradient, and proved Fick's first law. Comparing Equation (10.8) with Equation (10.2), it would appear that the diffusion coefficient is given by $D = \frac{1}{2} \lambda <v>$. In actual fact, the approximations we have made in reaching Equation (10.8) mean that this is not quite correct (within a distance λ from our window, some molecules are lost through collisions, an effect which needs to be corrected for), and a more rigorous treatment yields

$$D = \frac{1}{3} \lambda <v> \qquad (10.9)$$

We can use this result to predict the way in which the rate of diffusion will respond to changes in temperature and pressure. Increasing the temperature will increase $<v>$, and therefore increase the diffusion rate, while increasing the pressure will reduce λ, leading to a reduction in the diffusion rate.

Thermal conductivity

We can derive equation (10.3), and obtain a value for the coefficient of thermal conductivity, κ, using a similar approach to that used above for diffusion. We will again consider the flux of molecules upon an imaginary window from the left and right, but this time we will assume that the gas has a uniform number density (no concentration gradient), but instead has a temperature gradient, with the temperature decreasing from left to right. We will assume that the average energy of a molecule is $\varepsilon = \alpha k_B T$, where α is the appropriate fraction given by the equipartition theorem (for example, a monatomic gas has $\alpha = 3/2$ and $\varepsilon = 3/2\, k_B T$). Using similar arguments to those above for diffusion, namely that molecules are on average reaching the window from a distance of one mean free path away, from regions in which their energies are $\varepsilon(-\lambda)$ and $\varepsilon(+\lambda)$, we obtain for the energy fluxes from left and right

$$J_L = \frac{1}{4} <v> n\, \varepsilon(-\lambda) = \frac{1}{4} <v> n\, \alpha\, k_B \left(T - \lambda \left(\frac{dT}{dz} \right)_0 \right)$$

$$J_R = \frac{1}{4} <v> n\, \varepsilon(+\lambda) = \frac{1}{4} <v> n\, \alpha\, k_B \left(T + \lambda \left(\frac{dT}{dz} \right)_0 \right) \qquad (10.10)$$

The net energy flux is therefore

$$J_z = J_L - J_R = -\frac{1}{2} \alpha \lambda <v> k_B n \left(\frac{dT}{dz} \right)_0 \qquad (10.11)$$

Again, this is not quite correct, and the true flux differs from this by a factor of 2/3 i.e.

$$J_z = -\frac{1}{3} \alpha \lambda <v> k_B n \left(\frac{dT}{dz} \right)_0 \qquad (10.12)$$

We have shown that the energy flux is proportional to the temperature gradient, and we can determine that the coefficient of thermal conductivity is given by

$$\kappa = \frac{1}{3} \alpha \lambda <v> k_B n \qquad (10.13)$$

We can simplify this slightly by recognising that for an ideal gas, the heat capacity at constant volume is given by $C_v = \alpha\, k_B\, N_A$. Substituting this into the above yields

$$\kappa = \frac{1}{3} \lambda <v> C_v [A] \qquad (10.14)$$

where $[A] = n/N_A = N/(N_A V)$ is the molar concentration. Note that because $\lambda \propto 1/p$ and $[A] \propto p$, the thermal conductivity is independent of pressure[2].

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[2] This is true at all but very low pressures. At extremely low pressures, the mean free path becomes larger than the dimensions of the container, and the container itself starts to influence the distance over which energy may be transferred.

Viscosity

Carrying out a similar treatment to those above for diffusion and thermal conductivity, we assume that molecules incident on our imaginary window from the left carry momentum $p_x(-\lambda) = mv_x(-\lambda)$ and those from the right carry momentum $mv_x(+\lambda)$. Our fluxes are now

$$J_L = \frac{1}{4}<v>n\ mv_x(-\lambda) = \frac{1}{4}<v>n\left(mv_x(0) - m\lambda\left(\frac{dv_x}{dz}\right)_0\right)$$

$$J_R = \frac{1}{4}<v>n\ mv_x(+\lambda) = \frac{1}{4}<v>n\left(mv_x(0) + m\lambda\left(\frac{dv_x}{dz}\right)_0\right) \qquad (10.15)$$

The net flux of momentum p_x along z is therefore

$$J_z = J_L - J_R = -\frac{1}{2}nm\lambda<v>\left(\frac{dv_x}{dz}\right)_0 \qquad (10.16)$$

Again we need to correct this expression by a factor of 2/3 to give

$$J_z = -\frac{1}{3}nm\lambda<v>\left(\frac{dv_x}{dz}\right)_0 \qquad (10.17)$$

The flux is proportional to the velocity gradient, as required, and we see that the coefficient of viscosity is given by

$$\eta = \frac{1}{3}nm\lambda<v> = \frac{1}{3}m\lambda<v>N_A[A] \qquad (10.18)$$

As was the case for thermal conductivity, the viscosity is independent of the pressure. However, it has a $T^{1/2}$ dependence on temperature through the mean velocity $<v>$. Note that this means that, unlike a liquid, the viscosity of a gas *increases* with temperature, since the increased velocity of the gas particles increases the momentum flux. In the gas phase we are able to neglect intermolecular forces to a good approximation, but in a liquid these forces have a major effect. The reason for the reduction in viscosity with increasing temperature in a liquid is that most of the energy goes into overcoming intermolecular forces, thereby making it easier for the molecules to move past each other.