The gas laws

Equations of state

The state of any sample of substance is specified by giving the values of the following properties:

V – the volume the sample occupies

p – the pressure of the sample

T – the temperature of the sample

n – the amount of substance in the sample

Experimental fact – these four quantities are not independent from one another. If we select the amount, the volume, and the temperature, then we find that we have to accept a particular pressure.

The substance obeys an **equation of state**, an equation in the form

$$p = f(n,V,T)$$

that relates one of the four properties to the other three.

The equations of state of most substances are not known. However, the equation of state of a low-pressure gas is known and proves to be very simple and useful. This equation is used to describe the behavior of gases taking part in reactions, the behavior of the atmosphere, as a starting point for problems in chemical engineering, and even in description of the structure of stars:

$$pV = nRT$$

The individual gas laws
Boyle's law (1661):

At constant temperature, the pressure of a fixed amount of gas is inversely proportional to its volume: $$p \propto 1/V$$

Consistent with the perfect gas equation of state. By treating n and T as constant, it becomes pV = constant. If we compress a fixed amount of gas at constant temperature into half of its original volume, then its pressure will double.

The graph is obtained by plotting experimental values of p against V for a fixed amount of gas at different temperatures and the curves predicted by Boyle's law. Each curve is called an **isotherm** because it depicts the variation of a property (in this case, the pressure) at a single constant temperature.
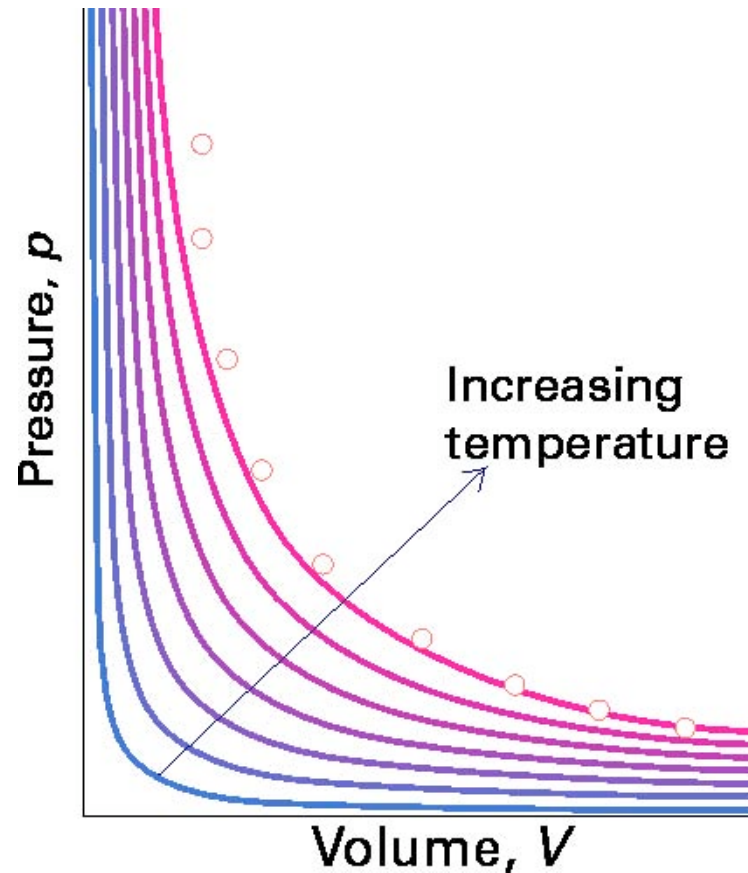
Experimental verification of Boyle's law

A good test of Boyle's law is to plot the pressure against $1/V$ (at constant temperature), when a straight line should be obtained. This diagram shows that the observed pressures approach a straight line as the volume is increased and the pressure reduced. A perfect gas would follow the straight line at all pressures; real gases obey Boyle's law in the limit of low pressures.
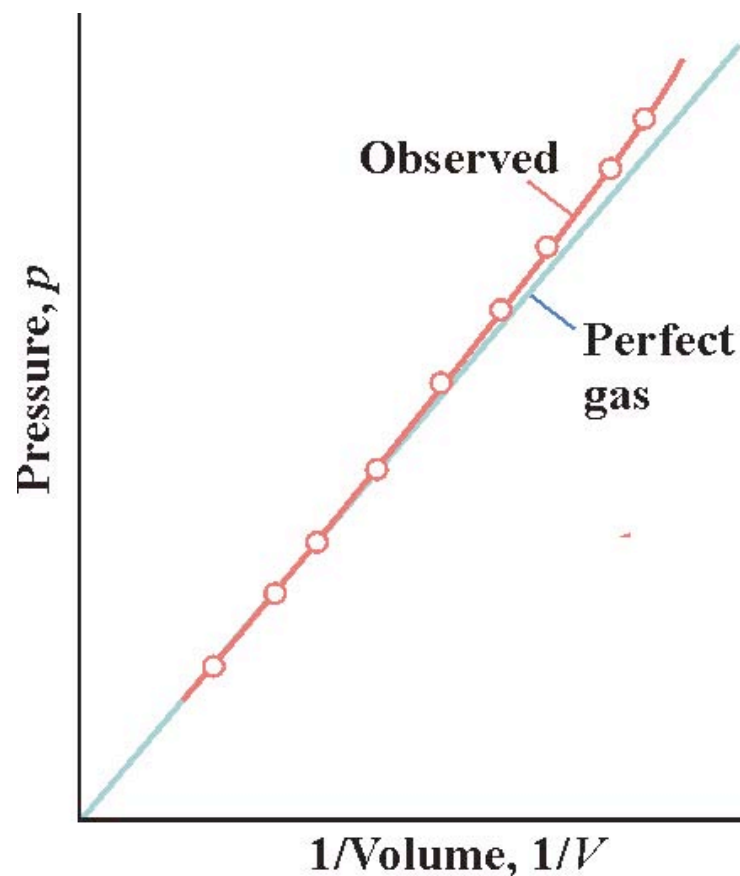
Charles's law (Gay-Lussac's law):

At constant pressure, the volume of a fixed amount of gas varies linearly with the temperature: $V = \text{constant} \times (\theta + 273.15)$

θ - the temperature on the Celsius scale.

Typical plots of volume against temperature for a series of samples of gases at different pressures. At low pressures and for temperatures that are not too low the volume varies linearly with the Celsius temperature. All the volumes extrapolate to zero as θ approaches the same very low temperature (-273.15 ºC). A volume cannot be negative – this common temperature must represent the **absolute zero** of temperature, a temperature below which it is impossible to cool an object. The Kelvin scale ascribes the value T = 0 to this absolute zero of temperature.

Charles's law takes the simpler form:

At constant pressure, $V \propto T$.

$V = \text{constant} \times T$ (at constant pressure)

$$V = nRT/p$$
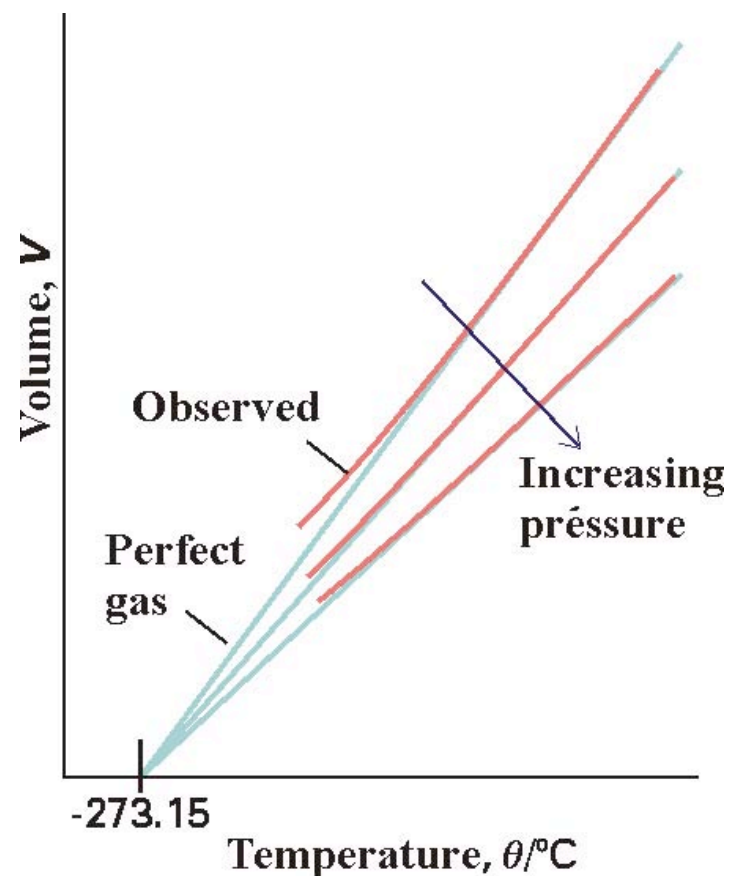
An alternative version of Charles's law, in which the pressure of a sample of gas is monitored under conditions of constant volume, is

$$p = \text{constant x } T \quad \text{(at constant volume)}$$

Avogadro's principle

At a given temperature and pressure, equal volumes of gas contain the same numbers of molecules.

If we double the number of molecules but keep the temperature and pressure constant, then the volume of the sample will double.

Avogadro's principle: at constant temperature and pressure, $V \propto n$

This result follows from the perfect gas law by treating p and T as constants. Avogadro's suggestion is a principle rather than a law (a direct summary of experience) because it is based on a model of a substance, in this case as a collection of molecules.

The **molar volume**, V_m, of any substance is the volume the substance occupies per mole of molecules.

Molar volume = (volume of sample) / (amount of substance) $\qquad V_m = V / n$

Avogadro's principle implies – the molar volume of a gas should be the same for all gases at the same temperature and pressure:

Perfect gas	24.7897 L mol^{-1}	Ammonia	24.8	Argon	24.4
Carbon dioxide	24.6	Nitrogen	24.8	Oxygen	24.8
Hydrogen	24.8	Helium	24.8		

The perfect gas law

The empirical observations summarized by Boyle's and Charles's laws and Avogadro's principle can be combined into a single expression:

$$pV = \text{constant} \times nT$$

The constant of proportionality was found experimentally to be the same for all gases, is denoted R and called **gas constant**.

$R =$ 8.31451 K^{-1} mol^{-1}

8.31451 kPa L K^{-1} mol^{-1}

8.20578 $\times$ 10^2 L atm K^{-1} mol^{-1}

62.364 L Torr K^{-1} mol^{-1}

1.98722 cal K^{-1} mol^{-1}

$$pV = nRT -$$ the **perfect gas equation**.

The most important equation in the whole of physical chemistry because it is used to derive a wide range of relations used throughout thermodynamics.

Perfect gas law – idealization of the equations of state that gases actually obey. All gases obey the equation ever more closely as the pressure is reduced towards zero. Example of a **limiting law** – a law that becomes increasingly valid as the pressure is reduced and is obeyed exactly in the limit of zero pressure.

A hypothetical substance which obeys the perfect gas law – **perfect gas**. Real gas behaves more and more like a perfect gas as its pressure is reduced. Atmospheric pressure (100 kPa) – most gases behave almost perfectly.

The gas constant R can be determined by evaluating $R = pV/nT$ for a gas in the limit of $p \rightarrow 0$. A more accurate value can be obtained by measuring the speed of sound in a low-pressure gas and extrapolating its value to zero pressure.
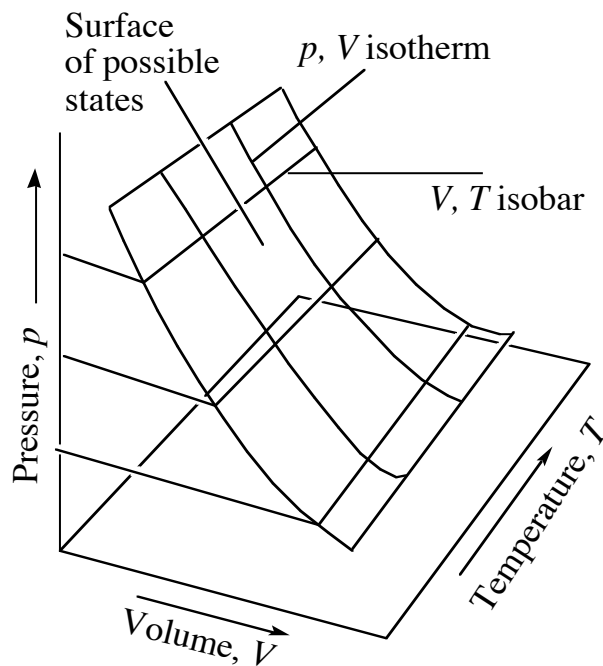
A plot of the pressure of a fixed amount of perfect gas against its volume and thermodynamic temperature. The surface depicts only possible states of a perfect gas: the gas cannot exist in states that do not correspond to points on the surface.

Using the perfect gas law

Example 1

A chemist is investigating the conversion of atmospheric nitrogen to usable form by a bacteria and needs to know the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 mL at 20ºC.

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

$$p = \frac{(1.25/28.02)mol \times (8.31451 kPaLK^{-1}mol^{-1}) \times (20 + 273.15K)}{0.250L}$$

$$= 435 kPa$$

$$n_{N_2} = \frac{m}{M_{N_2}} = \frac{1.25g}{28.02 gmol^{-1}} = \frac{1.25}{28.02} mol \quad T/K = 20 + 273.15$$

Example 2

We are given the pressure under one set of conditions and are asked to predict the pressure of the same sample under a different set of conditions.

$$\frac{p_1 V_1}{T_1} = nR \qquad \frac{p_2 V_2}{T_2} = nR \qquad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Combined gas equation

Using the combine gas equation

In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at 100 atm and 300 K, what pressure would it exert at the working temperature if it behaved as a perfect gas?

$$V_1 = V_2 \qquad \frac{p_1}{T_1} = \frac{p_2}{T_2} \qquad p_2 = \frac{T_2}{T_1} \times p_1 \qquad p_2 = (500 \text{ K} / 300 \text{ K}) \times (100 \text{ atm}) = 167 \text{ atm}$$

Example 3

How to use the perfect gas equation to calculate the molar volume of a perfect gas at any temperature and pressure?

$$V = \frac{nRT}{p} \qquad V_m = \frac{V}{n} = \frac{nRT}{np} = \frac{RT}{p}$$

For a given temperature and pressure all gases have the same molar volume.

It is convenient to report data in chemical research at a particular set of standard conditions. **Standard ambient temperature and pressure** (SATP) – a temperature of 25°C (more precisely, 298.15 K) and a pressure of 1 bar.

The **standard pressure** of 1 bar is denoted $p^{\varnothing}$: $\qquad\qquad\qquad p^{\varnothing} = 1$ bar exactly

The molar volume of a perfect gas at SATP – 24.79 L mol^{-1}. This value implies that at SATP 1 mol of perfect gas occupies about 25 L.

An earlier set of standard conditions – **standard temperature and pressure** (STP) - 0°C and 1 atm. The molar volume of a perfect gas at STP – 22.41 L mol^{-1}.

Altitude, h/km
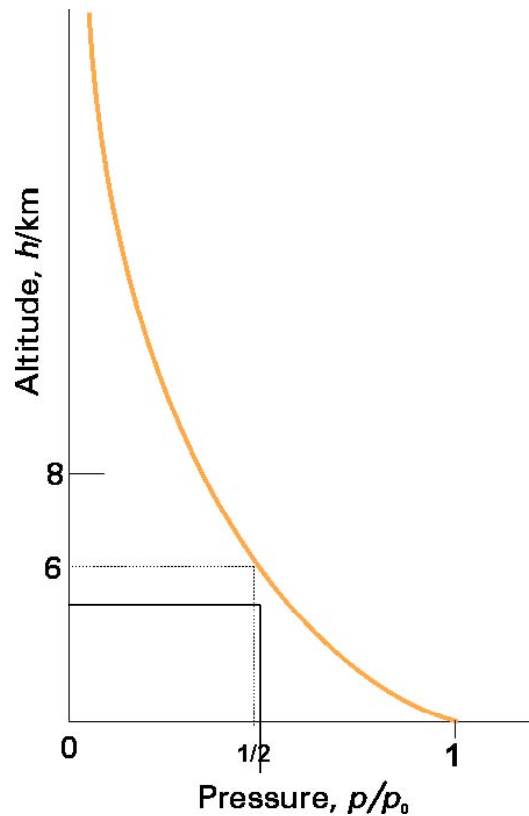
Pressure, p/p₀

The gas laws and the atmosphere

The biggest sample of gases accessible to us is the atmosphere. Its composition is maintained moderately constant by diffusion and convection (winds, local turbulence – eddies) but the pressure and temperature vary with altitude and the local conditions. One of the most variable constituents is water vapor – humidity. From Avogadro's principle – the presence of water vapor results in a lower density of air at a given temperature and pressure (the molar mass of H_2O is 18 g mol^{-1}, the average molar mass of air molecules is 29 g mol^{-1}.

The pressure and temperature vary with altitude. In the troposphere the average temperature is 15°C at sea level, falling to 57 °C at 11 km. At Kelvin scale: T ranges from 288 to 216 K, an average of 268 K.

Supposing that the temperature has its average value all the way up to 11 km, the pressure varies with altitude, h, according to the *barometric formula*: $p = p_0\exp(-h/H)$

p_0 – the pressure at sea level

H – a constant, approximately 8 km, $H=RT/Mg$ M – the average molar mass of air.

The pressure of the air and its density fall to half their sea level value at $h = H \ln 2$, 6 km.

Mixture of gases: partial pressures

Dalton's law: *The pressure exerted by a mixture of perfect gases is the sum of pressures that each gas would exert if it were alone in the container at the same temperature:*

$$p = p_A + p_B + \ldots$$

p_J – the pressure that a gas J would exert if it were alone in the container at the same temperature. For each gas: $\quad\quad p_J = n_J RT/V$

Dalton's law is strictly valid only for mixtures of perfect gases but it can be treated as valid for most conditions we encounter.

Suppose we were interested in the composition of inhaled and exhaled air and we knew that a certain mass of carbon dioxide exerts a pressure of 5 kPa when present alone in a container and that a certain mass of oxygen exerts 20 kPa when present alone in the same container. Then, when both gases are present in the container, the carbon dioxide in the mixture contributes 5 kPa to the total pressure and oxygen contributes 20 kPa; according to Dalton's law, the total pressure of the mixture is the sum of these two pressures, 25 kPa.
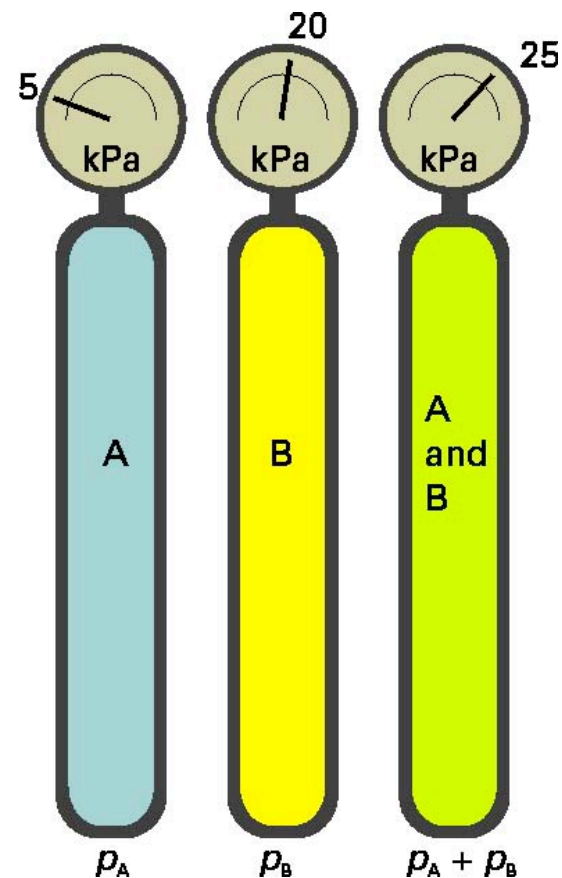
For any type of gas in a mixture, the **partial pressure**, p_J, is defined as $\quad p_J = x_J \times p$ x_J – the **mole fraction** of J in the mixture. The mole fraction of J is the amount of J molecules expressed as a fraction of the total amount of molecules in the mixture.

In a mixture that consist of n_A A molecules, n_B B molecules, and so on, the mole fraction of J is

Mole fraction of J = (amount of J molecules)/
$\qquad\qquad$ (total amount of molecules)

☐A ☐B

$x_J = n_J/n, \quad n = n_A + n_B + \dots$

$x_A = 0.167$
$x_B = 0.833$

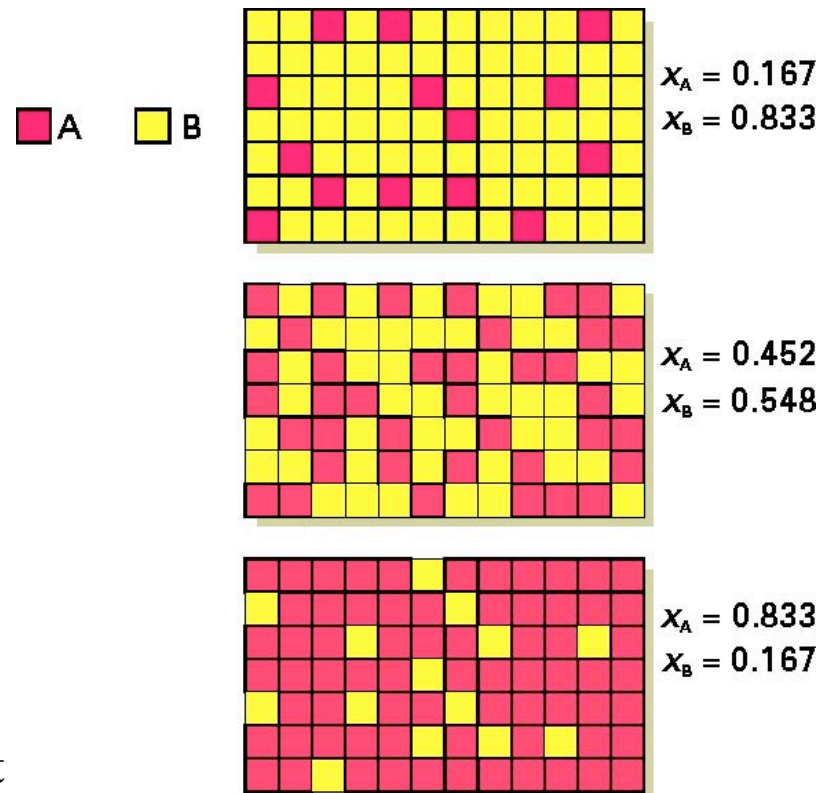For a **binary mixture** consisting of two species:
$\quad x_A = n_A/(n_A + n_B) \quad x_B = n_B/(n_A + n_B) \quad x_A + x_B = 1$

$x_A = 0.452$
$x_B = 0.548$

For a mixture of perfect gases, we can identify the partial pressure of J with the contribution that J makes to the total pressure. Using $p = nRT/V$,
$\quad p_J = x_J \times nRT/V = n_J RT/V$

$x_A = 0.833$
$x_B = 0.167$

The value of $n_J RT/V$ is the pressure that an amount n_J of J would exert in the otherwise empty container.

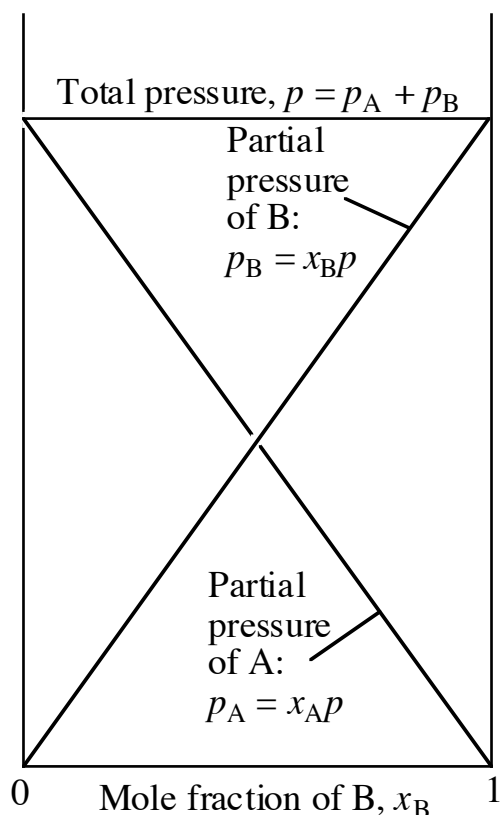From the definition of x_J, whatever the composition of the mixture,

$$x_A + x_B + \ldots = 1$$
$$p_J = x_J \times p$$

Therefore,

$$p_A + p_B + \ldots = (x_A + x_B + \ldots)p = p$$

This relation is true for both real and perfect gases.

The partial pressures p_A and p_B of a binary mixture of (real or perfect) gases of total pressure p as the composition changes from pure A to pure B. The sum of the partial pressures is equal to the total pressure. If the gases are perfect, then the partial pressure is also the pressure that each gas would exert if it were present alone in the container.

Example 4. Using Dalton's law

A container of volume 10.0 L holds 1.00 mol N_2 and 3.00 mol H_2 at 298 K. What is the total pressure in atmospheres if each component behaves as a perfect gas?

$$p = p_A + p_B = (n_A + n_B)\, RT/V$$

Use $R = 8.206 \times 10^{-2}$ L atm K^{-1} mol^{-1}.

$p = (1.00$ mol $+ 3.00$ mol$)\ 8.206 \times 10^{-2}$ L atm K^{-1} mol^{-1} × (298 K) / 10.0 L

$$p = 9.78 \text{ atm}$$

Total pressure, $p = p_A + p_B$

Partial pressure of B:
$p_B = x_B p$

Partial pressure of A:
$p_A = x_A p$

0   Mole fraction of B, x_B 1

Example 5. Calculating partial pressures

The mass percentage composition of dry air at sea level is approximately N_2: 75.5; O_2: 23.2; Ar: 1.3. What is the partial pressure of each component when the total pressure is 1 atm?

We expect species with a high mole fraction to have a proportionally high partial pressure, as partial pressures are defined by $p_J = x_J \times p$. To calculate mole fractions, we use the fact that the amount of molecules J of molar mass M_J in a sample of mass m_J is $n_J = m_J / M_J$. The mole fractions are independent of the total mass of the sample, so we can choose the latter to be 100 g (for simplicity of calculations).

$n(N_2) = 0.755 \times 100 \text{ g} / 28.02 \text{ g mol}^{-1} = 2.69 \text{ mol}$

$n(O_2) = 0.232 \times 100 \text{ g} / 32.00 \text{ g mol}^{-1} = 0.725 \text{ mol}$

$n(Ar) = 0.013 \times 100 \text{ g} / 39.95 \text{ g mol}^{-1} = 0.033 \text{ mol}$

$n = n(N_2) + n(O_2) + n(Ar) = 3.448 \text{ mol}$

$x(N_2) = n(N_2) / n = 2.69 \text{ mol} / 3.448 \text{ mol} = 0.780$

$x(O_2) = n(O_2) / n = 0.725 \text{ mol} / 3.448 \text{ mol} = 0.210$

$x(Ar) = n(Ar) / n = 0.033 \text{ mol} / 3.448 \text{ mol} = 0.0096$

$p(N_2) = x(N_2) \times p = 0.780 \times 1 \text{ atm} = 0.780 \text{ atm}$

$p(O_2) = x(O_2) \times p = 0.210 \times 1 \text{ atm} = 0.210 \text{ atm}$

$p(Ar) = x(Ar) \times p = 0.0096 \times 1 \text{ atm} = 0.0096 \text{ atm}$

We have not had to assume that the gases are perfect: p_J are defined as $p_J = x_J \times p$ for any kind of gas.

# The kinetic model of gases: three assumptions –

1. A gas consists of molecules in ceaseless random motion.
2. The size of the molecules is negligible in the sense that their diameters are much smaller that the average distance traveled between collisions.
3. The molecules do not interact, except during collisions –

   The potential energy of the molecules is independent of their separation and may be set to zero. The total energy of a sample of gas is the sum of the kinetic energies of all molecules present in it. The faster the molecules travel, the greater the total energy of the gas.

The point-like molecules move randomly with a wide range of speeds and in random directions, both of which change when they collide with the walls or with other molecules.

The pressure of a gas according to the kinetic model

The kinetic theory accounts for the steady pressure exerted by a gas in terms of the collisions the molecules make with the walls of the container. Each collision gives rise to a brief force on the wall but, as billions of collisions take place every second, the walls experience a virtually constant force, and hence the gas exerts a steady pressure.
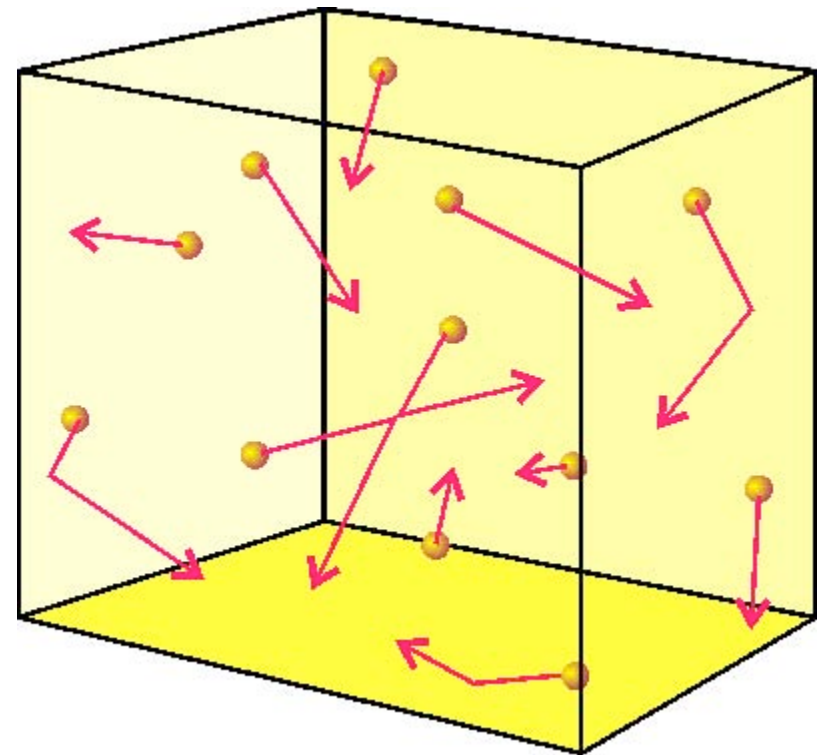
The pressure exerted by a gas of molar mass M in a volume V is $$p = \frac{nMc^2}{3V}$$

c – the **root-mean-square speed** (r.m.s. speed) of the molecules: $$c = \left(\frac{s_1^2 + s_2^2 + \ldots + s_N^2}{N} \right)^{1/2}$$

The r.m.s. speed enters kinetic theory naturally as a measure of the average kinetic energy of the molecules. The kinetic energy of a molecule of mass m traveling at a speed v is $E_k = \frac{1}{2} mv^2$, so the mean kinetic energy is the average of this quantity, $\frac{1}{2} mc^2$.

Therefore, $$c = \left(\frac{2E_k}{m} \right)^{1/2}.$$

The r.m.s. speed is quite close in value to the **mean speed**, $\bar{c}$: $$\bar{c} = \frac{s_1 + s_2 + \ldots + s_N}{N}$$

For samples consisting of large numbers of molecules, $$\bar{c} = \left(\frac{8}{3\pi} \right)^{1/2} c \approx 0.921c$$

The equation for the pressure can be written as $$pV = \frac{1}{3} nMc^2$$

which resembles $pV = nRT$.

The average speed of gas molecules

$$\frac{1}{3}nMc^2 = nRT \qquad\qquad c = \left(\frac{3RT}{M}\right)^{1/2}$$

At 25°C, an r.m.s. speed for oxygen and nitrogen molecules can be calculated as 482 and 515 m s^{-1}, respectively. Both these values are not far off the speed of sound in air (346 m s^{-1} at 25°C).

The r.m.s. speed of molecules in a gas is proportional to the square root of the temperature.

Doubling the temperature (on the Kelvin scale) increases the mean and the r.m.s. speed of molecules by a factor of $2^{1/2} = 1.414\ldots$

The Maxwell distribution of speeds

Not all molecules travel at the same speed: some move more slowly than the average, and the others may briefly move at much higher speed than the average. There is a ceaseless redistribution of speeds among molecules as they undergo collisions. Each molecule collides once every nanosecond (1 ns $= 10^{-9}$ s) or so in a gas under normal conditions.

Distribution of molecular speeds – Maxwell distribution of speeds

The fraction f of molecules that have a speed in a narrow range between s and $s+\Delta s$

is $\qquad\qquad f = F(s)\Delta s \qquad$ with $\qquad F(s) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} s^2 e^{-Ms^2/2RT}$

1. Because f is proportional to Δs, the fraction in the range Δs increases in proportion to the width of the range. If at a given speed the range increases (but remains narrow), then the fraction in that range increases in proportion.

2. The equation includes a decaying exponential function (a function in the form e^{-x}, with x proportional to s^2). This implies that the fraction of molecules with very high speed will be very small.

3. The factor $2M/RT$ multiplying s^2 in the exponent is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. Heavy molecules are unlikely to be found with very high speed.

$$F(s) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} s^2 e^{-Ms^2/2RT}$$

4. The opposite is true when the temperature, T, is high: then the factor $2M/RT$ in the exponent is small, so the exponential factor falls towards zero relatively slowly as s increases. At high temperatures, a greater fraction of the molecules can be expected to have high speeds than at low temperatures.

5. A factor s^2 (the term before the exponent) multiplies the exponential. This factor goes to zero as s goes to zero, so the fraction of molecules with very low speed will also be very small.

The remaining factors form the normalization factor – ensure that, when we add together the fractions over the entire range of speeds from zero to infinity, we get 1.

Maxwell distribution of speeds and its variation with the temperature

Only small fractions of molecules have very low or very high speeds. The fraction with very high speeds increases sharply as the temperature is raised, as the tail of the distribution reaches up to higher speeds. This feature plays an important role in the rates of gas-phase chemical reactions because the rate of a reaction depends on the energy of collision – on their speeds.
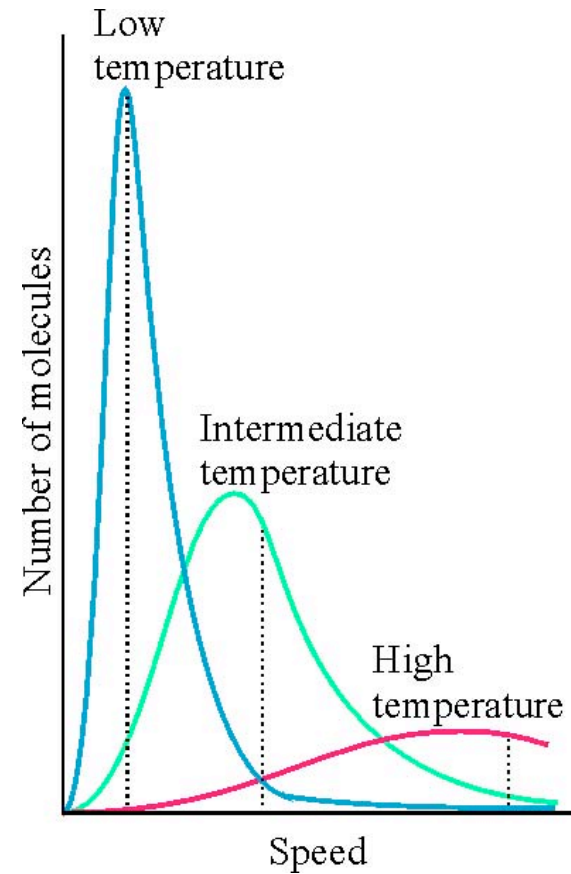
Maxwell distribution of speeds depends on the molar mass of the molecules

Not only do heavy molecules have lower average speeds than light molecules at a given temperature, but they also have a significantly narrower spread of speeds. That narrow spread means that most molecules will be found with speeds close to average. In contrast, light molecules (H_2) have high average speed and a wide spread of speeds – many molecules will be found traveling either much faster or much slower than the average – composition of planetary atmospheres.
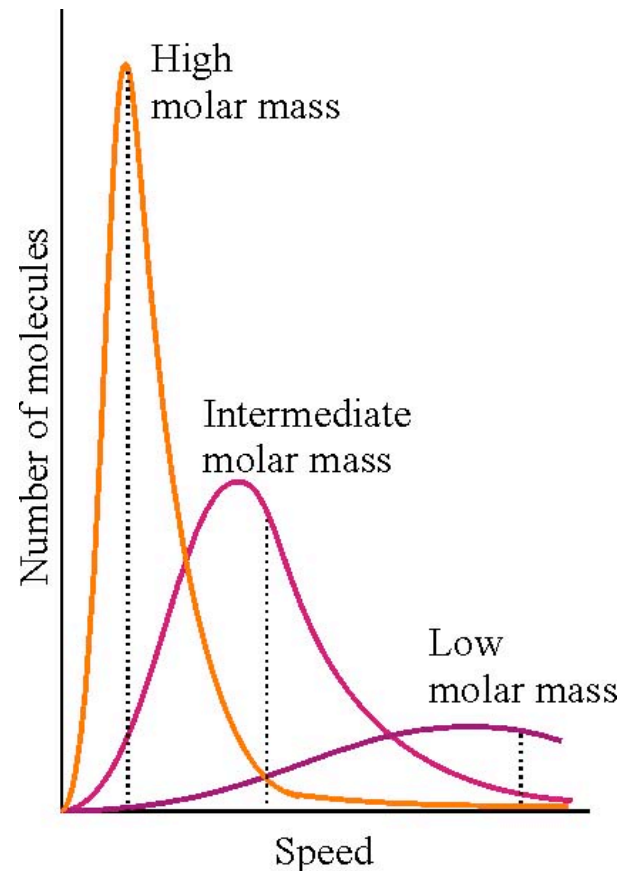
Molecular collisions

Mean free path, λ - the average distance that a molecule travels between collisions. In gases – several hundred molecular diameters.

Collision frequency, z – the average rate of collisions made by one molecules, the average number of collisions one molecules makes in a time interval divided by the length of the interval. The inverse of the collision frequency, $1/z$, is the **time of flight** – the average time that a molecule spends in flight between two collisions.

The mean free path and the collision frequency are related by

c = (mean free path)/(time of flight) = λ / (1/z) = λ z

To find expressions for λ and z we need to suppose that the molecules are not simply point-like; to obtain collisions we need to assume that two 'point' score a hit whenever they come within a certain range d of each other; d – diameter.

The **collision cross-section**, σ, the target area presented by one molecule to another: $\sigma = \pi d^2$

$$\lambda = \frac{RT}{2^{1/2} N_A \sigma p} \qquad z = \frac{2^{1/2} N_A \sigma c p}{RT}$$

1. Because $\lambda \propto 1/p$, the mean free path decreases as the pressure increases – a result of the increase in the number of molecules present in a given volume as the pressure increased, so each molecule travels a shorter distance before it collides with a neighbor.

2. Because $\lambda \propto 1/\sigma$, the mean free path is shorter for molecules with large collision cross-sections.

3. Because $z \propto p$, the collision frequency increases with the pressure of the gas – provided the temperature is the same, each molecule takes less time to travel to its neighbor in a denser, higher-pressure gas.

4. Because $z \propto c$ and $c \propto 1/M^{1/2}$, providing their collision cross-sections are the same, heavy molecules have lower collision frequencies than light molecules. Heavy molecules travel more slowly on average than light molecules do (at the same temperature), so they collide with other molecules less frequently.
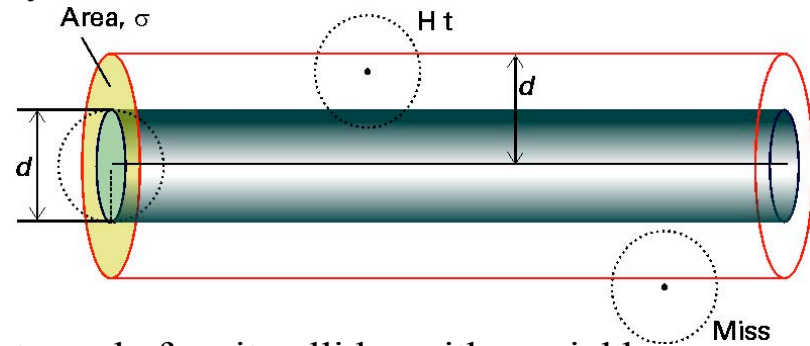
Real Gases

Real gases do not obey the perfect gas law exactly. Deviations from the law are particularly important at high pressures and low temperatures, especially when a gas is on the point of condensing to liquid. Real gases deviate from the perfect gas law because molecules interact with each other. Repulsive forces between molecules assist expansion and attractive forces assist compression.

Intermolecular interactions

At relatively long distances (a few molecular diameters) molecules attract each other – condensation of gases into liquids at low temperatures. At low enough T, the molecules of a gas have insufficient kinetic energy to escape from each other's attraction and they stick together.

As soon as the molecules come into close contact they repel each other – liquids and solids have a definite bulk and do not collapse to an infinitesimal point.

Intermolecular interactions – potential energy that contributes to the total energy of the gas. Attractions – negative contribution, repulsions – positive contribution.

At large separations, the energy-lowering interactions are dominant, but at short distances the energy-raising repulsions dominate.

The intermolecular interactions affect the bulk properties of the gas.

At high pressure, when the average separation of the molecules is small, the repulsive forces dominate and the gas can be expected to be less compressible because now the forces help to drive the molecules apart.
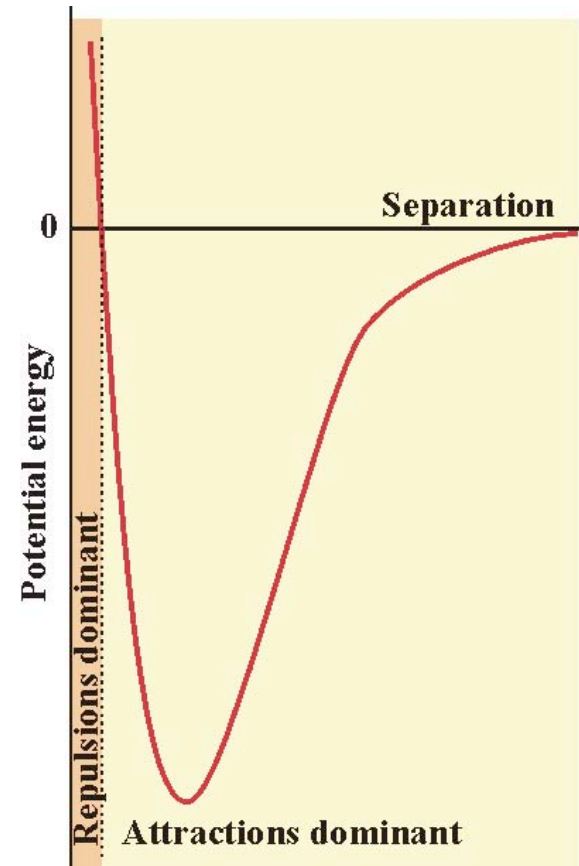
The isotherms of real gases

The isotherms of real gases have shapes different from those implied by Boyle's law. Although the experimental isotherms resemble the perfect gas isotherms at high temperature (and at low pressures), there are very striking differences at temperatures below about 50ºC and at pressures about 1 bar.

Consider isotherm at 20ºC. At point A the sample is a gas. As the sample is compressed to point B by pressing in a piston, the pressure increases broadly in agreement with Boyle's law, the increase continues until point C. Beyond this point, the piston can be pushed in without any further increase in pressure, through D to E. The reduction in volume from E to F requires a very large increase in pressure.

The gas at C condenses to a compact liquid at E. If we could see the sample, we would see it begin to condense to a liquid at C, and the condensation would be complete when the piston was pushed in to E. At E, the piston is resting on the surface of the liquid. The subsequent reduction in volume from E to F corresponds to the very high pressure needed to compress a liquid. The pressure corresponding to the line CDE, when both liquid and vapor are in equilibrium, is called the **vapor pressure** of the liquid at the temperature of the experiment.

The step from C to E – the molecules are so close on average that they attract each other and cohere into a liquid.

The step from E to F – trying to force the molecules even closer together when they are already in contact – trying to overcome strong repulsive interactions between them.
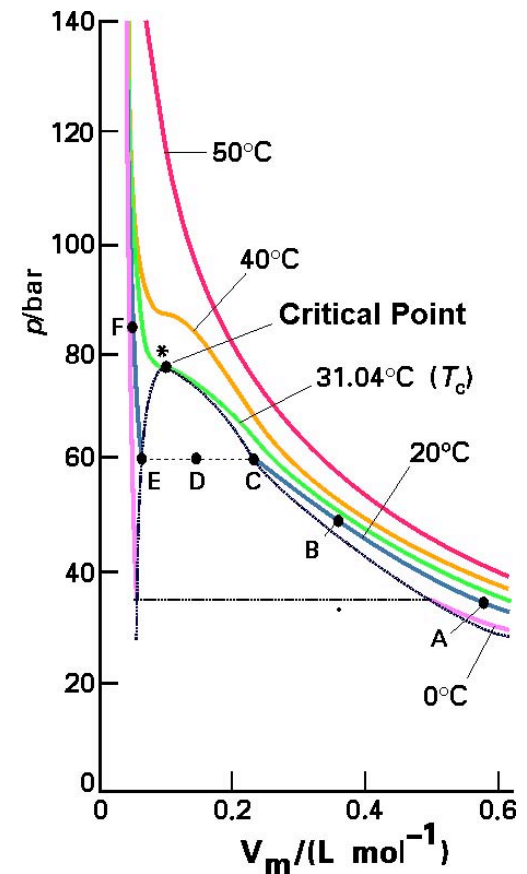
The compression factor

The compression factor, Z – the ratio of the actual volume of a gas to the molar volume of a perfect gas under the same conditions.

Compression factor = (molar volume of gas)/(molar volume of perfect gas)

$Z = V_m/V_m(\text{perfect})$

$Z = V_m/(RT/p) = pV_m/RT$ For a perfect gas, $Z = 1$.

When Z is measured for real gases, it is found to vary with pressure. At low pressures, some gases (methane, ethane, and ammonia, for instance) have $Z<1$. Their molar volumes are smaller than that of a perfect gas – the molecules cluster together slightly – the attractive interactions are dominant.

The compression factor rises above 1 at high pressures for any gas and for some gases (H_2) $Z>1$ at all pressures. $Z>1$ – the molar volume of the gas is now greater than that expected for a perfect gas of the same temperature and pressure – dominant repulsive forces.

These forces drive the molecules apart when they are forced to be close together at high pressures.

For hydrogen, the attractive interactions are so weak that the repulsive interaction dominate even at low pressures.
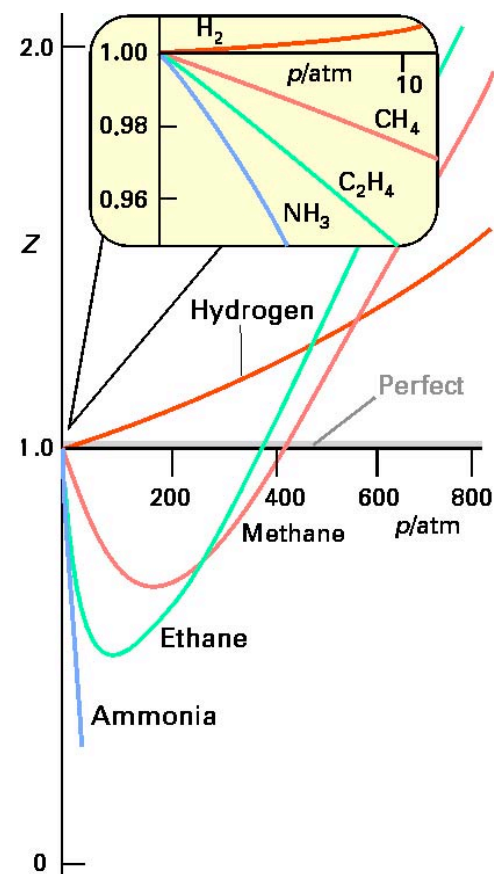
The virial equation of state

The deviation of Z from 1 can be used to construct and *empirical* (observational) equation of state. We suppose that, for real gases, the relation $Z = 1$ is only the first term of a lengthier equation:

$$Z = 1 + B'p + C'p^2 + ... \quad \text{or} \quad Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ...$$

B, C, … - **virial coefficients** – vary from gas to gas and depend on the temperature.

This technique, of taking a limiting expression and supposing that it is the first term of a more complicated expression, is quite common in physical chemistry.

The limiting expression is the first approximation to the true expression, whatever that may be, and the additional terms take into account secondary effects that the limiting expression ignores.

B – the most important additional term. Positive for hydrogen but negative for methane, ethane, and ammonia.

Regardless of the sign of B, the positive term C/V_m^2 becomes large at high pressures and Z becomes greater than 1.

The values of the virial coefficients for many gases are known from measurements of Z over a range of pressures and fitting the data to the equation.

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + ... \qquad p = \frac{nRT}{V}\left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + ...\right) \qquad \text{the \textbf{virial equation of state}}$$

At very low pressures, when the molar volume is very large, the terms B/V_m and C/V_m^2 are both very small, and only the 1 inside the parentheses survive. In this limit (of p approaching 0), the equation of state approaches that of a perfect gas.

Although the equation of state of a real gas may coincide with those of the perfect gas law as $p \rightarrow 0$, not all of its properties necessarily coincide with those of a perfect gas in that limit. Consider dZ/dp – the slope of the graph of compression factor against pressure. For a perfect gas:

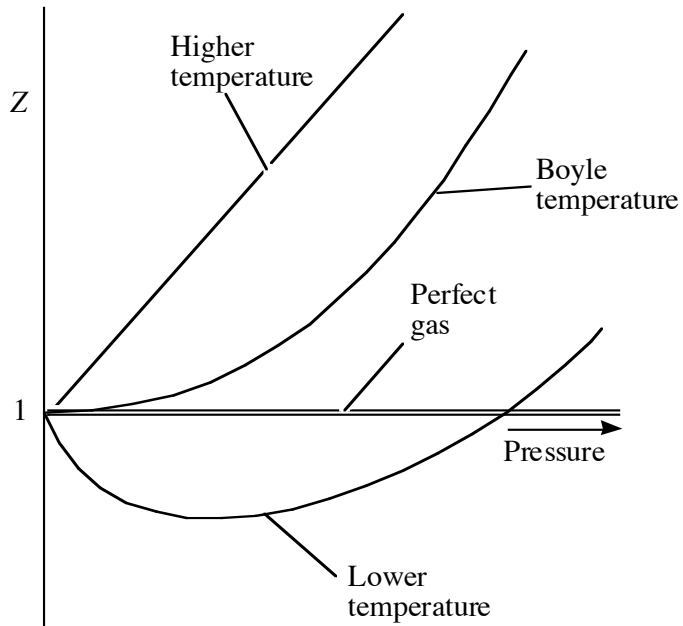$$Z = 1 \qquad \Rightarrow \qquad dZ/dp = 0 \text{ always}$$

For a real gas:

$$Z = 1 + B'p + C'p^2 + \ldots$$
$$\frac{dZ}{dp} = B' + 2pC' + \ldots \rightarrow B' \qquad \text{as} \qquad p \rightarrow 0$$

B' is not necessarily 0, so the slope of Z with respect to p does not necessarily approach 0 (the perfect gas value). Because several properties depend on derivatives, the properties of real gases do not always coincide with the perfect gas values at low temperatures. Similarly,

$$\frac{dZ}{d(1/V_m)} \rightarrow B \quad \text{as } V_m \rightarrow \infty, \text{ corresponding to } p \rightarrow 0$$

Virial coefficients depend on temperature $\Rightarrow$ there may be a temperature at which $Z \to 1$ with zero slope at low p or high V_m – **Boyle temperature** T_B.
Z has a zero slope as $p \to 0$ if $B = 0 \Rightarrow$
$B = 0$ at Boyle temperature.
Then, $pV_m \approx RT_B$ over a more extended range of pressures than at other T, because the B/V_m term in the virial equation is zero and higher terms are negligibly small. $T_B = 22.64$ K for He, 364.8 K for air.

The critical temperature

If we look inside the container at point D, we would see the liquid separated from the remaining gas by a sharp surface. At a slightly higher T, a liquid forms but at a higher pressure. It might be more difficult to make out the surface – the remaining gas is at such a high pressure that its density is similar to that of the liquid. At the special T (31.04°C or 304.19 K for CO_2) the gaseous state transforms continuously into the condensed state and at no stage is there a visible surface between the two states of matter.

At **critical temperature**, T_c, and at all higher temperatures, a single form form of matter fills the container at all stages of the compression and there is no separation of a liquid from the gas. *A gas cannot be condensed to a liquid by the application of pressure unless the temperature is below the critical temperature. T_c, critical pressure p_c, critical molar volume V_c* - critical constants of a substance, define the critical point of the gas.

Critical temperature/°C

He	-268	Ne	-229
Ar	-123	Kr	-64
Xe	17	Cl_2	144
Br_2	311	H_2	-240
O_2	-118	H_2O	374
N_2	-147	NH_3	132
CO_2	31	CH_4	-83
CCL_4	283	C_6H_6	289
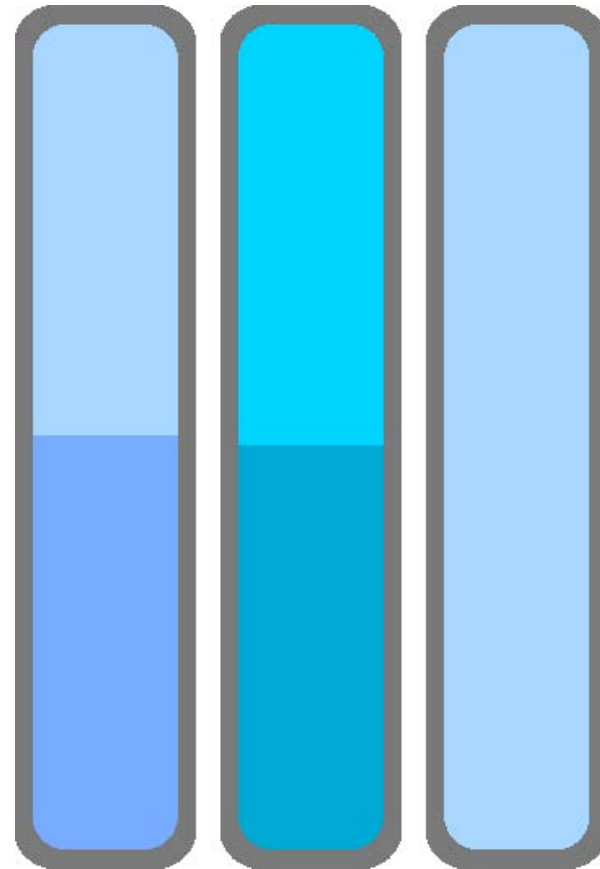
The dense fluid obtained by compressing a gas at $T>T_c$ is not a true liquid, but it behaves like a liquid – has a similar density and can act as a solvent – **supercritical fluid.** Supercritical fluids are currently being used as solvents.

The van der Waals equation of state

   Proposed in 1873 – and approximate equation of state – shows how the intermolecular interactions contribute to the deviations of a gas from the perfect gas law. The repulsive interaction implies that the molecules cannot come closer than a certain distance. Instead of being free to travel anywhere in a volume V, the actual volume is reduced to an extent proportional to the number of molecules present and the volume they each exclude – change V with $V-nb$, b – the proportionality constant.
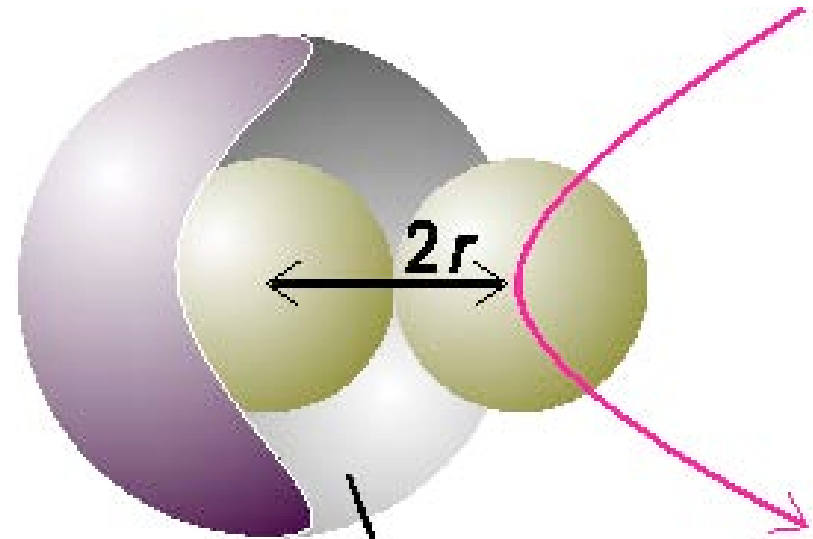
$$p = nRT/(V-nb)$$

When the pressure is low, the volume is large compared with the excluded volume – nb can be ignored – perfect gas equation of state.

Attractive interactions – the attraction experienced by a given molecule is proportional to the concentration, n/V. The attractions slow the molecules down – the molecules strike the walls less frequently and with a weaker impact – the reduction of pressure is proportional to the square of the molar concentration, one factor of n/V reflecting the reduction in frequency of collision and the other factor the reduction in the strength of their impulse.

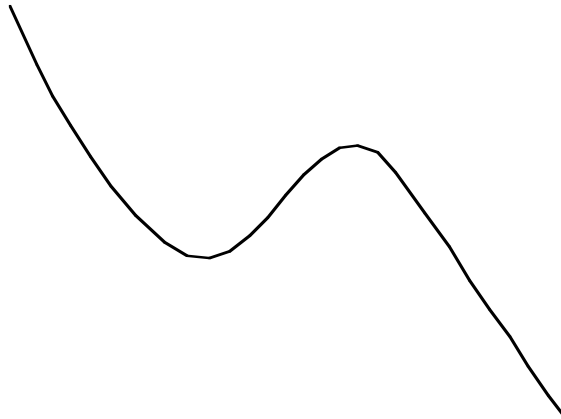Reduction in pressure $= a \times (n/V)^2$

van der Waals equation of state:

van der Waals parameters a and b are known for many gases (independent of T).
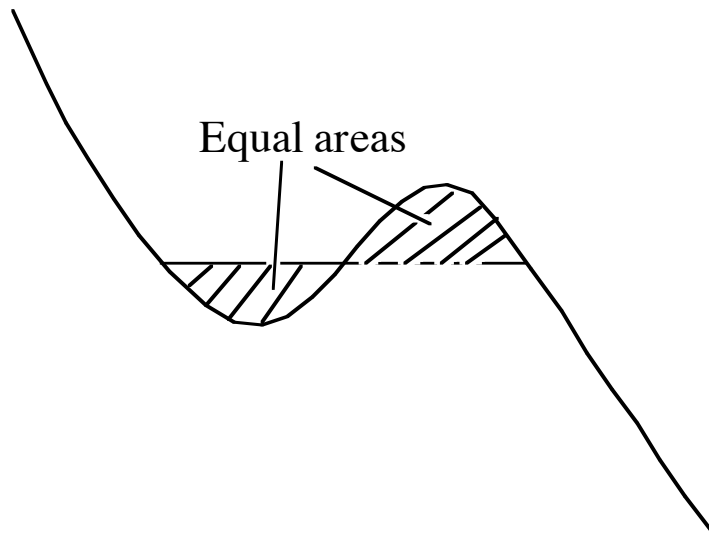

2 r

Excluded volume

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

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

The reliability of the van der Waals equation

We can judge the reliability of the equation by comparing the isotherms it predicts with the experimental isotherms. At $T > T_c$ the calculated isotherms resemble experimental ones. But below T_c they show unrealistic oscillations.

Equal areas

The oscillations (**van der Waals loops**) are unrealistic because they suggest that under some conditions an increase of pressure results in an increase of volume. Therefore, they are replaced by horizontal lines drawn so the loops define equal areas above and below the lines: the **Maxwell construction**.

The van der Waals coefficients are found by fitting the calculated curves to experimental ones.

The features of the equation

(1) Perfect gas isotherms are obtained at high temperatures and large molar volumes.

When the temperature is high, RT may be so large that the first term in $p = \dfrac{RT}{V_m - b} - \dfrac{a}{V_m^2}$

greatly exceeds the second. If the molar volume is large, $V_m \gg b$, then $V_m - b \approx V_m$. Under these conditions, the equation reduces to the perfect gas equation.

(2) Liquids and gases coexist when cohesive and dispersing effects are in balance.

The van der Waals loops occur when both terms in the equation have similar magnitudes. The first term arises from the kinetic energy of the molecules and their repulsive interactions; the second represents the effect of the attractive interactions.

(3) The critical constants are related to the van der Waals coefficients.

For $T < T_c$, the calculated isotherms oscillate and pass through a minimum followed by a maximum. These extrema converge and coincide at $T = T_c$; at the critical point the curve has a flat inflexion:
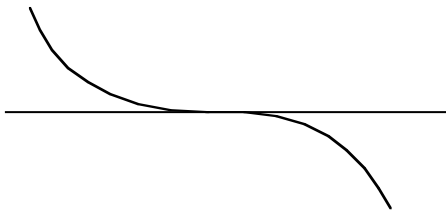
Mathematically, such inflexion occurs when the first and second derivatives are zero:

$$\frac{dp}{dV_m} = -\frac{RT}{(V_m - b)^2} + \frac{2a}{V_m^3} = 0 \qquad \frac{d^2 p}{dV_m^2} = \frac{2RT}{(V_m - b)^3} - \frac{6a}{V_m^4} = 0$$

$$V_c = 3b \qquad p_c = a / 27b^2 \qquad T_c = 8a / 27Rb$$

$Z_c = p_c V_c / RT_c = 3/8$ for all gases: the **critical compression factor**

The principle of corresponding states

The critical constants are characteristic properties of real gases $\Rightarrow$ a scale can be set up by using these constants. We introduce the **reduced variables**: $p_r = p/p_c$ $V_r = V_m/V_c$ $T_r = T/T_c$
Hope: gases confined to the same reduced volume, V_r, at the same reduced temperature, T_r, would exert the same reduced pressure, p_r. The hope was largely fulfilled:
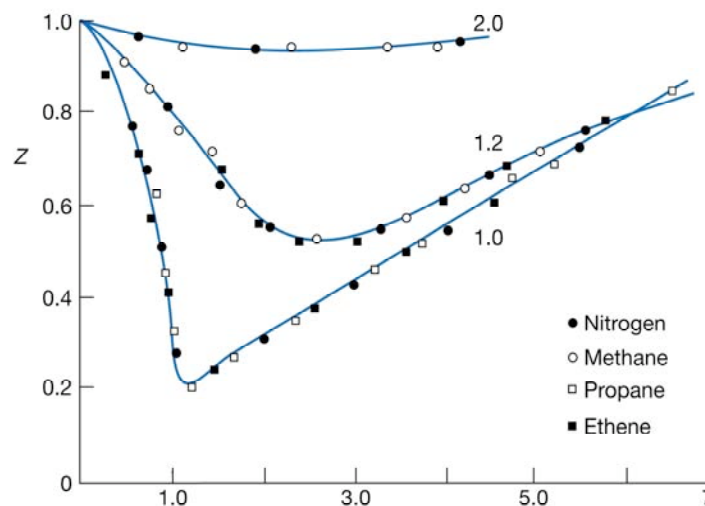
The **principle of corresponding states**: real gases at the same reduced volume and reduced temperature exert the same reduced pressure. Works best for gases composed of spherical molecules; fails when the molecules are non-spherical or polar.

$$\frac{ap_r}{27b^2} = \frac{8aT_r}{27b(3bV_r - b)} - \frac{a}{9b^2V_r^2} \qquad p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2}$$

a and b disappear

If isotherms are plotted in terms of the reduced variables, the same curves are obtained whatever the gas: the van der Waals equation is compatible with the principle of corresponding states.

Other equations of state also accommodate the principle; all we need are two parameters playing the roles of a and b and then the equations can be always manipulated into reduced form. This means that the effects of the attractive and repulsive interactions can each be approximated in terms of a single parameter.