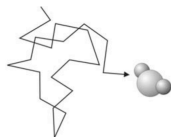


Properties Of Gases

We can use classical mechanics to describe the properties and behaviour of gases. As the interactions between gas particles are relatively weak, we can describe the gas phase using relatively simple models.

Characteristics of the Gas Phase

1. **A gas is a collection of particles in constant random motion.** The particles in a gas continually undergoing collisions with each other and with the walls of the container.
2. **A gas fills any container it occupies.** This is consistent with the second law of thermodynamics, gas expansion is a spontaneous process due to the accompanying increase in entropy.
3. **The effects of intermolecular forces in a gas are generally small.** For many gases over a wide range of temperatures and pressures, they can be ignored entirely.



States of Gases

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.

The **equation of state** for a gas is simply an expression that relates these four variables.

Gases & Vapours

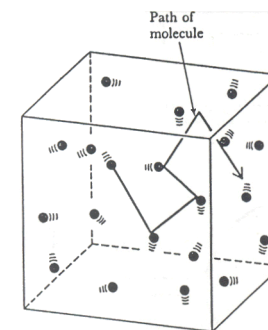
The difference between a 'gas' and a 'vapour' is sometimes a source of confusion. When a gas phase of a substance is present under conditions when the substance would typically be a solid or liquid then we call this a vapour phase.

For example, at the surface of a liquid an equilibrium exists between the liquid and gas phases. At a temperature below the boiling point of the substance, the gas is termed 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 boiling point is the temperature at which the vapour pressure of the substance is equal to the ambient pressure.

This is in contrast to a 'fixed gas', which is a gas for which no liquid or solid phase exists at the temperature of interest (e.g. gases such as N_2 , O_2 or He at room temperature).

Pressure

Pressure is a measure of the **force** exerted by a gas **per unit area**. In a gas, these force arise from collisions of the particles in the gas with the surface at which the pressure is being measured, often the walls of the container. The SI units of pressure is Newtons per square metre (Nm^{-2}), or Pascals (Pa). Several other units of pressure are in common usage (1 Torr = 1 mmHg = 133.3 Pa) (1 bar = 100 000 Pa).



Dalton's Law of Partial Pressures

As the measured pressure arises from collisions of individual gas particles with the container walls, 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**.

$$p = \sum_i p_i$$

We can also write this in terms of mole fractions, x_i

$$p_i = x_i p \quad \text{where} \quad x_i = \frac{n_i}{\sum_i n_i}$$

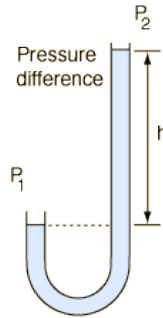
Barometric Pressure

Static fluid pressure is determined by the density and depth of a fluid. Consider a U-tube filled with a non-volatile liquid: One end of the tube provides a reference pressure (p_2) 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_1). 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 equilibrium, the liquid exerts a pressure,

$$\Delta p = -\rho g \Delta h$$

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.



An Example: $\Delta p = \rho g \Delta h$ Derivation

Consider the pressure exerted on the bottom of a column of fluid of height h and cross-sectional area A . The pressure p on this area is simply F/A . The force is $-mg$ (if 'up' is the positive direction of displacement, the force acts in the opposite direction). Given the mass density of the fluid is ρ , $m = \rho V$. So

$$p = -\frac{mg}{A} = -\frac{\rho V g}{A} = -\rho g h$$



An Example: Barometric Pressure

We can also use this formula to estimate how the pressure varies with height in the atmosphere. Assuming the atmosphere can be described by the perfect gas equation $pV = nRT$ (we will explore this equation in detail shortly) and that the mass density of the gas $\rho = M/V$, where M is the mass of volume V . We can show

$$p = p_0 e^{-\frac{mgh}{k_B T}}$$

where m is the mass of a gas particle.

We can write an expression for the density of gas in term of the the ideal gas equation

$$\rho = \frac{M}{V} = \frac{Mp}{nRT}$$

We know that $\Delta p = -\rho g \Delta h$ or alternatively, $dp = -\rho g dh$, so inserting our expression for the density

$$dp = -\rho g dh = -\frac{Mpg}{nRT} dh$$

If we assume M , n , ρ , g and T are all independent of h , we can solve this by separating variables and integrating

$$\int \frac{1}{p} dp = -\frac{Mg}{nRT} \int dh$$

giving

$$\ln \frac{p}{p_0} = -\frac{Mg}{nRT} h \quad \text{or} \quad p = p_0 e^{-\frac{Mg}{nRT} h} \quad \text{or} \quad p = p_0 e^{-\frac{M_p g}{RT} h}$$

Note that we have assumed that temperature doesn't change with height, which is clearly a radical approximation of the actual atmosphere!

Temperature

The temperature of a gas is a measure of the **kinetic energy** possessed by the particles in the gas. The temperature therefore reflects their velocity distribution. The velocity of any single particle within a gas changes 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. This velocity distribution will be covered in detail later.

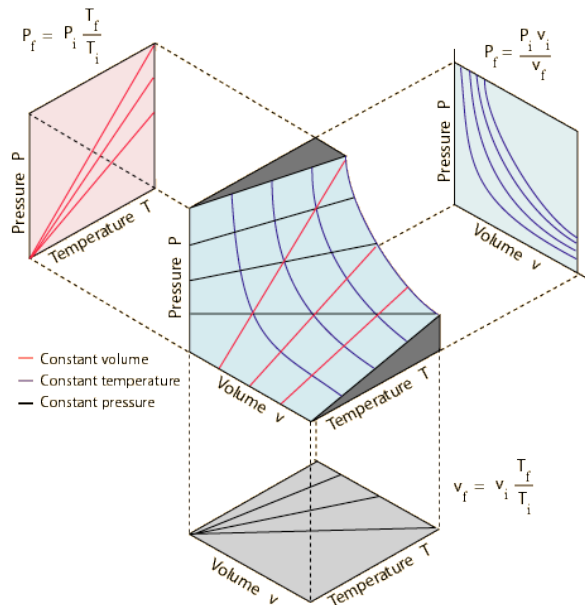
The Gas Laws

The perfect gas equation is an equation of state that can be used to describe the behaviour of a gas at low pressure.

$$pV = nRT$$

In this equation R is the molar gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. 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 empirical equation was established by combining a series of experimental results obtained from the seventeenth century onwards. All the possible states of an ideal gas can be represented on a three-dimensional pVT plot.⁴ The behaviour when any one of the three state variables is held constant is also shown.



We can rewrite the perfect gas equation as

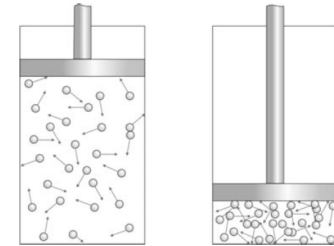
$$\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$$

Boyle's law

If the temperature is fixed, this equation becomes Boyle's law.

$$p_i V_i = p_f V_f$$

Consider the figure; when the plunger is depressed, the gas occupies a much smaller volume, and there are many more collisions with the inside surface of the plunger, increasing the pressure.



Charles' Law

If the pressure is constant, then the ideal gas law takes the form of Charles' Law

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

Pressure-temperature law

We can complete the set of law's by including the relation between pressure and temperature: For a fixed volume, the pressure of a gas is proportional to the absolute temperature of the gas.

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

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. For a fixed volume of gas, these factors combine to give an increase in pressure, and for fixed pressure, we must increase the volume.

⁴ Plot reproduced from <http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/idegas.html#c1>

Ideal Gases

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

1. **The gas consists of particles in constant random motion.**
2. **There are no intermolecular forces between the gas particles.**
3. **The separation of particles is large compared to particle diameter.** (i.e. the volume occupied by the particles is negligible compared to the volume of the container they occupy).
4. **The only interactions between the particles and with the container walls are perfectly elastic collisions.** Recall 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).

If a gas is ideal, its behaviour is described by

$$pV = nRT$$

Real Gases

In a real gas, the atoms or particles obviously do have a finite size, and at close range they do interact with each other through a variety of intermolecular forces. The ideal gas model breaks down under conditions of high pressure, when the particles are forced close together and therefore interact strongly, and at low temperatures, when the particles are moving slowly and intermolecular forces have a long time to act during a collision.

The Compression Factor, Z

The deviations of a real gas from ideal gas behaviour may be quantified by the compression factor, 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.

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

The value of Z tells us about the dominant types of intermolecular forces acting in a gas.

$Z = 1$ No intermolecular forces.

Ideal gas behaviour.

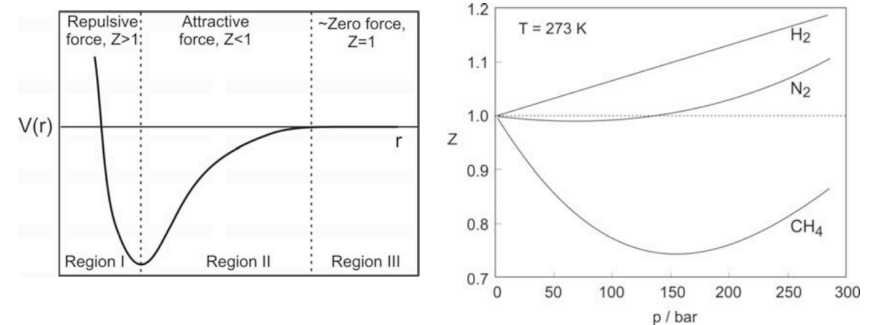
$Z < 1$ Attractive forces dominate.

Gas occupies a smaller volume than an ideal gas.

$Z > 1$ Repulsive forces dominate.

Gas occupies a larger volume than an ideal gas.

To understand the behaviour at higher pressures we can consider a typical intermolecular potential, $V(r)$. The value for Z depends on how this potential is sampled at a given pressure and temperature.

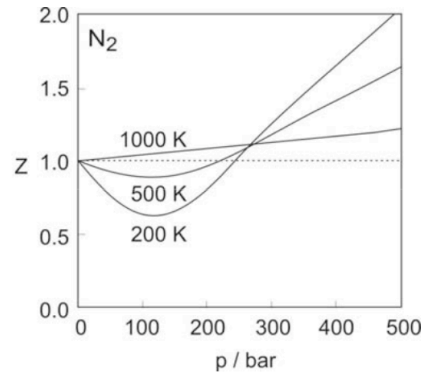


Region I. At very small separations electron cloud overlap gives rise to strong repulsive interactions. The particles take up a larger volume than they would in an ideal gas, and $Z > 1$.

Region II. As the particles approach each other, they experience an attractive interaction This reducing the molar volume such that $Z < 1$, in comparison to an ideal gas.

Region III. At large separations the interaction potential is effectively zero and $Z = 1$. When the particles are widely separated we therefore expect the gas to behave ideally, thus all gases approach $Z = 1$ at very low pressures.

The compression factor depends on temperature: (1) At higher speeds there is less time during a collision for the attractive part of the potential to act. (2) Higher energy collisions means that the particles penetrate further into the repulsive part of the potential during each collision, so the repulsive interactions become more dominant. The temperature of the gas therefore changes the balance between the contributions of attractive and repulsive interactions to the compression factor.



The pressure-dependent compression factor for N_2 at three different temperatures is shown above.

Equations of State for Real Gases

There are a number of ways in which the ideal gas equation may be modified to take account of the intermolecular forces present in a real gas.

Virial Expansion

One way is to treat the ideal gas law as the first term in an expansion of the form:

$$pV_m = RT(1 + B'p + C'p^2 + \dots)$$

This is known as a virial expansion, and the coefficients B' , C' etc are called **virial coefficients**. In many applications, only the first correction term is included.

Often, a more convenient form for the virial expansion is:

$$pV_m = RT \left(1 + \frac{B}{V} + \frac{C}{V^2} + \dots \right)$$

van der Waal's Equation of State

Another widely used equation for treating real gases is the **van der Waal's** equation. The van der Waal's equation of state attempts to account for the size of molecules and the attractive forces between molecules

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

a and b are temperature-independent coefficients; a accounts for the attractive forces and b describes the molar volume excluded by the particles