The Kinetic Theory Of Gases

General Description

The properties of a perfect gas can be understood by considering the random motion of the particles in the gas. The **kinetic theory of gases** provides a quantitative description of this behaviour. The kinetic theory of gases is based on the assumption that the only contribution to the energy of the gas is from kinetic energy.

Assumptions

Recall the assumptions used in describing a perfect gas

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.**

Derivation

We can construct an expression for the pressure of an ideal gas by applying Newton's laws of motion to the random motion of gas particles in a container of volume, V.

Our first task is to determine the force on the walls of the container. It is easiest to begin by considering the motion of a single particle in just one dimension.

The momentum change along the x co-ordinate during one elastic collision of a particle of mass, m is

$$\Delta p = p_{\text{after}} - p_{\text{before}} - = -mv_x - (mv_x) = -2mv_x$$

Since momentum must be conserved, the total momentum imparted to the wall must be $+2mv_x$.
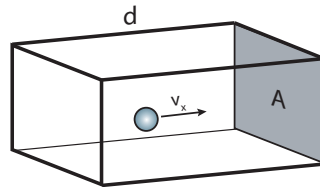
The time between collisions for this particle with the wall is simply

$$\Delta t = \frac{2d}{v_x}$$

As pressure is force per unit area, we can work out the force on the wall. From Newton's second law

$$F = ma = \frac{d(p)}{dt} \approx \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2d/v_x} = \frac{mv_x^2}{d}$$

So the pressure exerted by one particle is simply

$$p = \frac{F}{A} = \frac{mv_x^2}{Ad} = \frac{mv_x^2}{V}$$

Pressure obviously doesn't result just from the collisions of one particle in one dimension, but many particles moving in all 3 dimensions.

We can extend our result to cope with the average behaviour of N particles by multiplying our result by N.

In addition, particles clearly do not all travel with the same speed, rather there is a distribution of speeds. We must therefore replace v_x^2 with $<v_x^2>$, the average squared velocity in the x direction.

$$p = \frac{Nm \langle v_x^2 \rangle}{V}$$

As there are three dimensions in total, we can simplify things further by realising that the average squared velocity in the x direction must be the same as that in the y and z directions.

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

Our final expression for the pressure becomes

$$p = \frac{Nm \langle v^2 \rangle}{3V} \qquad \text{or} \qquad pV = \frac{1}{3} Nm \langle v^2 \rangle$$

equation is constant. You should recognise this as a form of **Boyle's law** (pV = constant).

To go further we can use the **equipartition theorem** to derive the ideal gas law, relating the above result to temperature. We will state the result here, before examining classical equipartition in more detail:

For each degree of freedom there is a ½$k_B T$ contribution to the internal energy

In our model, there are only three translational degrees of freedom that contribute to the internal energy. As all collisions are perfectly elastic in our model, the total internal energy must be equal to the kinetic energy of the particles. The average kinetic energy is just $½m\langle v^2\rangle$, therefore

$$\frac{3}{2}k_B T = \frac{1}{2}m\left\langle v^2\right\rangle$$

Substituting this into our original expression for the pressure

$$pV = \frac{1}{3}Nm\left\langle v^2\right\rangle$$

yields

$$pV = Nk_B T$$

where k_B is the Boltzmann constant. As $R = N_A k_B$ we can also write this as

$$pV = nRT$$

which is the perfect, or ideal, gas equation.

Classical Equipartition

We needed to use the theory of classical equipartition in our derivation the ideal gas equation. The equipartition theorem enables us to estimate the average energy of a system based upon the number of degrees of freedom of the system.

The mean energy of each quadratic contribution to the total energy of a particle is equal to ½$k_B T$	or	**For each degree of freedom there is a ½$k_B T$ contribution to the internal energy**

A quadratic contribution to the energy is one that is proportional to the square of a particle's velocity or position.

Degrees of Freedom

For any given molecule, the total number of degrees of freedom is given by *3N*, where N is the number of atoms.

The Classical Hamiltonian

To continue we need to calculate the total energy of a system; The total energy of a system can be described by its Hamiltonian. Classically, the Hamiltonian is simply the sum of all the contributions to the kinetic and potential energy of the system.

Translation

For purely translational motion, we have three degrees of freedom corresponding to x, y, and z directions of translational motion.

$$H = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

So we predict a 3⁄2 kBT contribution to the average energy of the system.

Rotation

For purely rotational motion of a particle, we would again predict three degrees of freedom corresponding to rotation about the x, y, and z axes.

$$H = \frac{1}{2}(I_x\omega_x^2 + I_y\omega_y^2 + I_z\omega_z^2)$$

However for linear particles such as diatomics, the moment of inertia about one of these axes, the molecular axis, is vanishingly small. Hence we predict a (2×½) $k_B T$

contribution to the average energy of the system for linear particles and a $3/2$ $k_B T$ contribution for non-linear particles.

Vibration

Vibrational motion of bonds have two contributions to the total energy; one from kinetic energy, and one from the potential energy. For example, for a one-dimensional harmonic oscillator

$$H = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

So for each vibration, we have two quadratic terms contributing to the total energy. We therefore predict a contribution of $k_B T$ to the total internal energy for each vibrational degree of freedom.

Summary

If there are *3N* degrees of freedom in total, subtracting the known number of translational and rotational degrees of freedom gives us $3N\text{-}5$ vibrational degrees of freedom for a linear particle and $3N\text{-}6$ vibrational degrees of freedom for a non-linear particle.

Heat Capacities and Equipartition

We know from thermodynamics that the heat capacity is related to the internal energy of a system

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

We can use the equipartition theorem to predict the average internal energy of a system, and hence predict the heat capacity.

	Contribution to C_v		
	trans.	rot.	vib.
monatomic	*3/2 R*	-	-
diatomic	*3/2 R*	*2/2 R*	*R*
linear	*3/2 R*	*2/2 R*	*(3N-5)R*
non-linear	*3/2 R*	*3/2 R*	*(3N-6)R*

This works surprisingly well for many gases (e.g. C_V for Argon is 12.47 JK⁻¹mol⁻¹). However, for many others it only functions reliably at high temperature. At low temperatures experimental heat capacities are much lower than those predicted by equipartition. Different degrees of freedom appear to be 'switched on' at different temperatures.
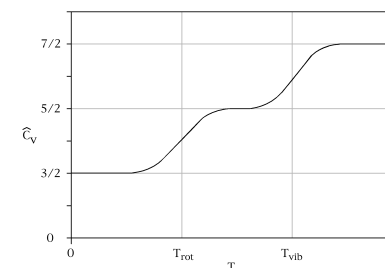
This can only be explained by associating each type of motion with a specific energy, and this requires quantum mechanics.