Experimentally observed properties of gases on which postulates of the theory are based

1. A gas expands to fill all the available space in its container.
   If the volume of container is increased, the gas will expand accordingly.
2. All gases expand rapidly into an evacuated container.
3. All gases diffuse freely into one another.
4. At equilibrium, all gases are distributed completely uniformly throughout their containers.
5. Gases have extremely low densities compared to liquids and to solids.
6. Gases are highly compressible compared to liquids and to solids.
7. If a fixed quantity of gas is left undisturbed at constant volume and at constant temperature, then the pressure of the gas remains constant indefinitely.

Postulates of the kinetic-molecular theory of gases

(Alternative *equivalent* statements are given for most of the postulates)

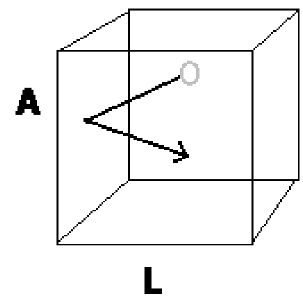
1. (a) A pure gas or a gas mixture is composed of an enormous number of molecules.
   (b) All properties of a gas that depend on statistical averages are well defined.
2. (a) The diameter of a molecule, or its largest dimension, is negligible compared to the average distance between the molecules in a gas.
   (b) The volume actually occupied by the molecules themselves is negligible compared to the volume of the gas, that is, the volume of the container.
   (c) Almost all of the volume occupied by a gas is empty space.
3. (a) The molecules of a gas are in constant rapid random motion.
   (b) On average, the number of gas molecules moving in any one direction is the same as the number of gas molecules moving in any other direction.
   (c) The distribution of molecular velocities is isotropic.
4. (a) The molecules in a gas exert no forces on one another.
   (b) The molecules in a gas neither attract nor repel one another.
   (c) The only energy of an ideal gas is kinetic energy. Ideal gases have no potential energy.
5. (a) The pressure that a gas exerts on the walls of its container is due to the collisions that the constantly moving molecules make with the walls.
   (b) The force that gas molecules exert on the walls of the container is due to the change in the linear momentum of the molecules as they bounce off the walls.
6. (a) All the collisions that the molecules make with the walls of the container, and all the collisons that the molecules make with one another, are completely elastic.
   (b) When a molecule in a gas strikes a wall of the container and rebounds, the angle of incidence equals the angle of reflection.
   (c) The total energy of the molecules of a gas remains constant so long as the temperature of the gas remains constant.
7. The effect of gravity on the molecules of a gas is completely negligible.

Simple physical reasoning leads to a major conclusion about gases obeying the above postulates:

8. The absolute temperature of a sample of an ideal gas is directly proportional to the average translational kinetic energy of the gas molecules.
   For such gases $PV = nRT$, the ideal gas law.

THE KINETIC THEORY OF GASES **Chemistry BC2001x**

Consider one molecule, flying around a cube of length L. We first wish to find the contribution of *this* molecule to the pressure. Focus on the collisions it makes with the left wall, defined by $x = 0$. The area of this wall is A.



Newton's second law says $\mathbf{F} = m\mathbf{a}$ where **F** and **a** are vectors. We will focus on the component of motion along the x direction (the axis perpendicular to the wall). Thus

$$F_x = ma_x$$

Acceleration a is the change in velocity: $a = (\Delta u/\Delta t)$. The collision with the wall is elastic, so the **speed** is unchanged. The velocity goes from $-u_x$ to $+u_x$, so $\Delta u = 2u_x$.

In what time interval Δt does the change in velocity occur? The molecule must travel the length of the box L and back before it hits this wall again:

distance = (speed) × (time) → time = distance/speed. Thus $\Delta t = 2L_x/u_x$.

→ $F = ma = m\,(2u_x)/(2L_x/u_x) = m\,u_x^2/L_x$.

Pressure = Force/Area = $m\,u_x^2/L_xA$

But $L_xA = V$, so $P = m\,u_x^2/V$

This is the contribution of this one molecule (with speed u_x) to the pressure.

Now we add the contributions of *all* molecules: n moles or nN_A molecules:

$$(P_1 + P_2 + ...) = P = (m/V)\,(u_{x1}^2 + u_{x2}^2 + ...) \quad \text{with } nN_A \text{ terms.}$$

The definition of an average of k terms c_i is $\langle c \rangle = (c_1 + c_2 + ..)/k \rightarrow (c_1 + c_2 + ..) = k\langle c \rangle$

thus $(u_{x1}^2 + u_{x2}^2 + ...) = nN_A\langle u_x^2 \rangle$.

Substituting: $P = nN_Am\langle u_x^2 \rangle/V$.

We have arrived at **Boyle's Law**: $PV = nN_Am\langle u_x^2 \rangle$. Everything on the right is constant.

For a single vector, the 3D version of the Pythagorean theorem says $u^2 = u_x^2 + u_y^2 + u_z^2$. The same is true for the average values: $\langle u^2 \rangle = \langle u_x^2 \rangle + \langle u_y^2 \rangle + \langle u_z^2 \rangle$. Since the motion of a molecule is a gas is isotropic, it is also true that $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$. Thus $\langle u^2 \rangle = 3\langle u_x^2 \rangle$.

→ $PV = nN_Am\langle u^2 \rangle/3$

In elementary physics, you learn that the kinetic energy of a particle $\varepsilon_K = \frac{1}{2} mu^2$ where u is the velocity. For a collection of particles $\langle \varepsilon_K \rangle = \frac{1}{2} m\langle u^2 \rangle$, so $m\langle u^2 \rangle = 2\langle \varepsilon_K \rangle$.

→ $PV = 2nN_A\langle \varepsilon_K \rangle/3$

The average kinetic energy per molecule multiplied by nN_A, the total number of molecules, is the total kinetic energy E_K. So $PV = (2/3)\,E_K$

The last postulate of the kinetic theory brings in the temperature: temperature is a measure of the average kinetic energy of the system, with kinetic energy **½RT** per degree of freedom per mole.

Thus for n moles and 3 degrees of freedom, $\mathbf{E_K = (3/2)nRT}$.

Finally: $\mathbf{PV = nRT}$

A related result: $E_K = (3/2)nRT = nN_A\langle \varepsilon_K \rangle = nN_Am\langle u^2 \rangle/2 \rightarrow 3RT = N_Am\langle u^2 \rangle = M\langle u^2 \rangle$

→ $\mathbf{\langle u^2 \rangle = 3RT/M}$ The mean square speed in a gas can be found from T and the molar mass M.