



Kinetic Theory of an Ideal Gas

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Abstract: Students will develop a model to describe that matter is made up of tiny particles, too small to be seen. Students will use the model to describe the differences in attraction among the particles of a solid, liquid, and gas. Finally, students will use their models of solids, liquids, and gases to explain their observations in the lesson.

Key words: Matter on Earth is in the form of solid, liquid, or gas.

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In a gas, the particles have very little attraction to each other. They are very far apart compared to the particles in a solid or liquid, and are constantly moving. The particles don't interact with one another but just hit and bounce off of each other when they collide. Ludwig Boltzmann, James Clerk Maxwell.

Kinetic theory of gases is based on the molecular picture of matter. A given amount of gas is a collection of a large number of molecules (typically of the order of Avogadro's number) that are in incessant random motion. At ordinary pressure and temperature, the average distance between molecules is a factor of 10 or more than the typical size of a molecule (2 \AA). Thus the interaction between the molecules is negligible and we can assume that they move freely in straight lines according to Newton's first law. However, occasionally, they come close to each other, experience intermolecular forces and their velocities change. These interactions are called collisions. The molecules collide incessantly against each other or with the walls and change their velocities. The collisions are considered to be elastic. We can derive an expression for the pressure of a gas based on the kinetic theory. We begin with the idea that molecules of a gas are in incessant random motion, colliding against one another and with the walls of the container. All collisions between molecules among themselves or between molecules and the walls are elastic. This implies that total kinetic energy is conserved. The total momentum is conserved as usual.

Pressure of an Ideal Gas Consider a gas enclosed in a cube of side l . Take the axes to be parallel to the sides of the cube, as shown in Fig. 1.4. A molecule with velocity (v_x, v_y, v_z) hits the planar wall parallel to yz -plane of area $A (= l^2)$. Since the collision is elastic, the molecule rebounds with the same velocity; its y and z components of velocity do not change in the collision but the x -component reverses sign. That is, the velocity after collision is $(-v_x, v_y, v_z)$. The change in momentum of the molecule is: $-mv_x - (mv_x) = -2mv_x$. By the principle of conservation of momentum, the momentum imparted to the wall in the collision $= 2mv_x$. To calculate the force (and pressure) on the wall, we need to calculate momentum imparted to the wall per unit time. In a small time interval Δt , a molecule with x -component of velocity v_x will hit the wall if it is within the distance $v_x \Delta t$ from the wall. That is, all molecules within the volume $Av_x \Delta t$ only can hit the

wall in time Δt . But, on the average, half of these are moving towards the wall and the other half away from the wall. Thus the number of molecules with velocity (v_x, v_y, v_z) hitting the wall in time Δt is $A v_x \Delta t n$ where n is the number of molecules per unit volume. The total momentum transferred to the wall by these molecules in time Δt is : $Q = (2mv_x) (n A v_x \Delta t)$ (1.1) The force on the wall is the rate of momentum transfer $Q/\Delta t$ and pressure is force per unit area : $P = Q/(A \Delta t) = n m v_x^2$ (1.2) Actually, all molecules in a gas do not have the same velocity; there is a distribution in velocities. The above equation therefore, stands for pressure due to the group of molecules with speed v_x in the x-direction and n stands for the number density of that group of molecules. The total pressure is obtained by summing over the contribution due to all groups: $P = n m \overline{v_x^2}$ (1.3) where $\overline{v_x^2}$ is the average of v_x^2 . Now the gas is isotropic, i.e. there is no preferred direction of velocity of the molecules in the vessel. Therefore, by symmetry, $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = (1/3) [\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}] = (1/3) \overline{v^2}$ (1.4) where v is the speed and $\overline{v^2}$ denotes the mean of the squared speed. Thus $P = (1/3) n m \overline{v^2}$ (1.5) some remarks on this derivation. First, though we choose the container to be a cube, the shape of the vessel really is immaterial. For a vessel of arbitrary shape, we can always choose a small infinitesimal (planar) area and carry through the steps above. Notice that both A and Δt do not appear in the final result. By Pascal's law, given in Ch. 10, pressure in one portion of the gas in equilibrium is the same as anywhere else. Second, we have ignored any collisions in the derivation. Though this assumption is difficult to justify rigorously, we can qualitatively see that it will not lead to erroneous results. The number of molecules hitting the wall in time Δt was found to be $n A v_x \Delta t$. Now the collisions are random and the gas is in a steady state. Thus, if a molecule with velocity (v_x, v_y, v_z) acquires a different velocity due to collision with some molecule, there will always be some other molecule with a different initial velocity which after a collision acquires the velocity (v_x, v_y, v_z). If this were not so, the distribution of velocities would not remain steady. In any case we are finding $\overline{v_x^2}$. Thus, on the whole, molecular collisions (if they are not too frequent and the time spent in a collision is negligible compared to time between collisions) will not affect the calculation above.

Founders of Kinetic Theory of Gases

James Clerk Maxwell (1831 – 1879), born in Edinburgh, Scotland, was among the greatest physicists of the nineteenth century. He derived the thermal velocity distribution of molecules in a gas and was among the first to obtain reliable estimates of molecular parameters from measurable quantities like viscosity, etc. Maxwell's greatest achievement was the unification of the laws of electricity and magnetism (discovered by Coulomb, Oersted, Ampere and Faraday) into a consistent set of equations now called Maxwell's equations. From these he arrived at the most important conclusion that light is an electromagnetic wave. Interestingly, Maxwell did not agree with the idea (strongly suggested by the Faraday's laws of electrolysis) that electricity was particulate in nature.

Ludwig Boltzmann (1844 – 1906) born in Vienna, Austria, worked on the kinetic theory of gases independently of Maxwell. A firm advocate of atomism that is basic to kinetic theory, Boltzmann provided a statistical interpretation of the Second Law of thermodynamics and the concept of entropy. He is regarded as one of the founders of classical statistical mechanics. The proportionality constant connecting energy and temperature in kinetic theory is known as Boltzmann's constant in his honour. © NCERT

$PV = (2/3) N \times m \overline{v^2}$ (1.5b) where $N (= nV)$ is the number of molecules in the sample. The quantity in the bracket is the average translational kinetic energy of the molecules in the gas. Since the internal energy E of an ideal gas is purely kinetic*, $E = N (1/2) m \overline{v^2}$ (1.6) Equation (1.7) then gives: $PV = (2/3) E$ (1.8) We are now ready for a kinetic interpretation of temperature. Combining Eq. (1.9) with the ideal gas Eq. (1.3), we get $E = (3/2) k_B N T$ (1.9) or $E/N = m \overline{v^2} = (3/2) k_B T$ (1.10) i.e., the average kinetic energy of a molecule is proportional to the absolute temperature of the gas; it is independent of pressure, volume or the nature of the ideal gas. This is a fundamental

result relating temperature, a macroscopic measurable parameter of a gas (a thermodynamic variable as it is called) to a molecular quantity, namely the average kinetic energy of a molecule. The two domains are connected by the Boltzmann constant. We note in passing that Eq. (1.11) tells us that internal energy of an ideal gas depends only on temperature, not on pressure or volume. With this interpretation of temperature, kinetic theory of an ideal gas is completely consistent with the ideal gas equation and the various gas laws based on it.

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