KINETIC THEORY OF GASES: PRESSURE, TEMPERATURE, AND MOLECULAR BEHAVIOR

This material covers fundamental concepts of the kinetic theory of gases, focusing on the relationship between molecular motion, pressure, and temperature, along with detailed distributions, collision phenomena, and energy principles.

CONCEPT OF PRESSURE AND TEMPERATURE

PRESSURE

According to the kinetic theory of gases, pressure exerted by an ideal gas is due to the continuous collisions of gas molecules with the walls of the container. Each collision imparts a momentum change to the wall, and the sum of these momentum changes per unit time and area results in the macroscopic pressure.

For an ideal gas, the pressure (P) is related to the average kinetic energy of the molecules by:

$P = (2/3) * (N/V) * KE_{avg}$

Where:

- N is the number of gas molecules.
- V is the volume of the container.
- KE_{avg} is the average kinetic energy per molecule.

TEMPERATURE

Temperature (T) is a direct measure of the average translational kinetic energy of the gas molecules. For an ideal gas, the relationship is:

$KE_{avg} = (3/2) * k_B * T$

Where:

- k_B is the Boltzmann constant (approximately 1.38 x 10^{-23} J/K).

Combining these, we get the ideal gas law in terms of kinetic theory: $PV = (1/3)N\, m\, v_{rms}^2 = N\, k_B\, T$, where v_{rms} is the root-mean-square speed.

NATURE OF DISTRIBUTION OF VELOCITIES (MAXWELL-BOLTZMANN DISTRIBUTION)

The Maxwell-Boltzmann distribution describes the statistical distribution of speeds of molecules in an ideal gas at a given temperature. Not all molecules move at the same speed; there is a range of speeds, and the distribution is not uniform.

ONE DIMENSION (1D)

The distribution function $f(v_x)$ for the velocity component along one axis (x) is a Gaussian distribution:

$f(v_x)dv_x = (m / (2\pi k_B T))^{1/2} \exp(-mv_x^2 / (2k_B T))\, dv_x$

TWO DIMENSIONS (2D)

The distribution of speeds in 2D, considering only speeds v, is:

$f(v)dv = (m / (k_B T)) * \exp(-mv^2 / (2k_B T)) * v\, dv$

THREE DIMENSIONS (3D)

The distribution of speeds in 3D is the most commonly used:

$f(v)dv = 4\pi\, (m / (2\pi k_B T))^{3/2} * v^2 \exp(-mv^2 / (2k_B T))\, dv$

From this distribution, we can derive characteristic speeds:

- **Most Probable Speed (v_p):** The speed at which the distribution function is maximum. $v_p = \mathrm{sqrt}(2k_B T / m) = \mathrm{sqrt}(2RT / M)$

- **Average Speed (v_{avg}):** The arithmetic mean of all speeds. $v_{avg} = \text{sqrt}(8k_BT / (\pi m)) = \text{sqrt}(8RT / (\pi M))$
- **Root Mean Square Speed (v_{rms}):** The square root of the mean of the squares of the speeds. $v_{rms} = \text{sqrt}(3k_BT / m) = \text{sqrt}(3RT / M)$

(Where R is the universal gas constant, and M is the molar mass.)

KINETIC ENERGY DISTRIBUTION

The distribution of kinetic energies (E) follows a similar pattern to velocity distribution, since $E = (1/2)mv^2$. The average kinetic energy is $KE_{avg} = (3/2)k_BT$.

The distribution function for kinetic energy per molecule is:

$f(E)dE = (2 / (\text{sqrt}(\pi) (k_BT)^{3/2})) * E^{1/2} \exp(-E / k_BT) dE$

COLLISIONS OF GAS MOLECULES

COLLISION DIAMETER (D)

The effective diameter of a molecule, representing the distance between the centers of two molecules at which they are considered to collide.

COLLISION NUMBER (Z)

The average number of collisions a single molecule makes per unit time.

MEAN FREE PATH (Λ)

The average distance traveled by a molecule between successive collisions.

$\lambda = 1 / (\text{sqrt}(2) * \pi * d^2 * (N/V))$

Alternatively, using the number density n = N/V:

$\lambda = 1 / (\mathrm{sqrt}(2) * \pi * d^2 * n)$

For a mixture of similar molecules, the factor sqrt(2) arises from the relative speed. For different molecules, it's more complex.

FREQUENCY OF BINARY COLLISIONS

SIMILAR MOLECULES

The collision frequency for a single molecule (Z_1) with other identical molecules is:

$Z_1 = \mathrm{sqrt}(2) * \pi * d^2 * v_{avg} * n$

The total number of collisions per unit volume per unit time (Z_{11}) between similar molecules is:

$Z_{11} = (1/2) * n * Z_1 = (1/\mathrm{sqrt}(2)) * \pi * d^2 * v_{avg} * n^2$

DIFFERENT MOLECULES

For a mixture of two types of molecules (1 and 2) with number densities n_1, n_2, diameters d_1, d_2, and average speeds v_{avg1}, v_{avg2}, the collision frequency of type 1 molecules with type 2 molecules (Z_{12}) is:

$Z_{12} = \pi * d_{12}^2 * v_{avg,rel} * n_2$

Where $d_{12} = (d_1+d_2)/2$ and $v_{avg,rel}$ is the average relative speed.

WALL COLLISION AND RATE OF EFFUSION

WALL COLLISION

The rate at which molecules strike a unit area of the container wall is proportional to the number density and the average molecular speed.

Rate of wall collisions per unit area = $(1/4) * n * v_{avg}$

RATE OF EFFUSION

Effusion is the process by which gas escapes through a small hole into a vacuum. The rate of effusion is proportional to the number of molecules striking the hole per unit time.

According to Graham's Law of Effusion, the rate of effusion of a gas is inversely proportional to the square root of its molar mass (or density) at constant temperature and pressure.

$\text{Rate}_1 / \text{Rate}_2 = \text{sqrt}(M_2 / M_1) = \text{sqrt}(\rho_2 / \rho_1)$

CALCULATION OF NUMBER OF MOLECULES WITH ENERGY ≥ E

The number of molecules with kinetic energy greater than or equal to a specific energy ε in 3D can be calculated by integrating the energy distribution function from ε to infinity:

$N(E \geq \varepsilon) = N * \int_{\varepsilon}^{\infty} f(E)dE$

For $E = (1/2)mv^2$, this integral often leads to expressions involving error functions or can be approximated.

PRINCIPLE OF EQUIPARTITION OF ENERGY

This principle states that for a system in thermal equilibrium, the total energy is shared equally among all its accessible degrees of freedom. Each degree of freedom contributes an average energy of $(1/2)k_BT$ per molecule.

APPLICATION TO MOLAR HEAT CAPACITY

The molar heat capacity (C_V) at constant volume is the amount of heat required to raise the temperature of one mole of a substance by one Kelvin. It is related to the internal energy (U) of the gas.

- **Monatomic gases** (e.g., He, Ne, Ar): 3 translational degrees of freedom. U = (3/2)$N_A k_B$T = (3/2)RT. C_V = dU/dT = (3/2)R.
- **Diatomic gases** (e.g., H_2, N_2, O_2) at moderate temperatures: 3 translational + 2 rotational degrees of freedom = 5 degrees of freedom. U = (5/2)RT. C_V = (5/2)R. (Vibrational modes are usually frozen out at room temperature).
- **Polyatomic gases**: Have more rotational and vibrational degrees of freedom.

The classical limit refers to the prediction from equipartition theorem before quantum mechanics corrected it for vibrational and rotational modes at very low temperatures.

NUMERICAL PROBLEMS

PROBLEM 1: SPEEDS OF OXYGEN MOLECULES

Calculate the most probable speed, average speed, and root-mean-square speed of oxygen molecules (M = 32 g/mol) at 27°C (300 K).

PROBLEM 2: MEAN FREE PATH

Consider nitrogen gas (N_2) at STP (0°C, 1 atm). Assume the diameter of a nitrogen molecule is approximately 3.7×10^{-10} m. Calculate the mean free path of a nitrogen molecule.

PROBLEM 3: EFFUSION RATE

A container with two gases, Helium (He) and Argon (Ar), at the same temperature and pressure, has a small hole. If Helium effuses out at a rate R_{He}, what will be the rate of effusion for Argon (R_{Ar})? (Molar mass of He ≈ 4 g/mol, Ar ≈ 40 g/mol).

PROBLEM 4: KINETIC ENERGY

What is the average kinetic energy of a single molecule of an ideal gas at 500 K?

PROBLEM 5: HEAT CAPACITY

For a diatomic gas, what is its molar heat capacity at constant volume (C_V) if only translational and rotational degrees of freedom are considered active? What would be its molar heat capacity at constant pressure (C_P)?

PROBLEM 6: WALL COLLISIONS

At 27°C, the number density of gas molecules in a container is 3×10^{25} m^{-3}. Calculate the rate at which molecules strike a unit area of the container wall.