

Chapter 31: Kinetic Molecular Theory

Predict the bimolecular rate constant of the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$ at 700.0 K using hard-core collision theory. Assume the hard-core collision radii are: $r_{\text{H}_2} = 1.1 \text{ \AA}$ and $r_{\text{I}_2} = 1.7 \text{ \AA}$.

Molecules must collide for a chemical reaction to occur. Not all collisions give successful reactions. Many reactions require the kinetic energy of the collision to exceed a threshold for a successful reaction to occur. The threshold is the activation energy, which is the collisional kinetic energy required to drive the bond breaking and making steps. In a gas, the collision rate depends on pressure and temperature. The kinetic energy of a gas molecule depends on temperature. The pressure, volume, and temperature relationships of a gas are determined by the equation of state. The classical theory of the pressure and kinetic energy relationships of ideal gases is called **kinetic molecular theory**, or **KMT**. Kinetic molecular theory is a necessary preliminary to classical and semi-classical theories of chemical reaction dynamics.

KMT was developed contemporaneously with thermodynamics. Thermodynamics and KMT provided the foundations of physical chemistry. The principles underlying KMT led to the development of statistical mechanics.

The pressure of a gas, the rate of collisions with a wall, and the rate of molecular collisions depend on the distribution of molecular speeds. Gas molecules travel with a wide range of molecular speeds, which on average are hundreds of meters per second. The distribution of molecular speed and translational kinetic energy are given by the Maxwell distribution. The Maxwell distribution can be derived using purely classical arguments. However, the derivation of the Maxwell distribution based on the Boltzmann distribution for the particle in a box brings together the core concepts of quantum mechanics and statistical mechanics. The result is a macroscopic theory of gas phase properties that is based on molecular theory.

31.1 The Pressure of a Gas is Determined by Molecular Motion

The goal is to understand P, V, T relationships in ideal gases and the rates of molecular collisions. What are the simplest assumptions that are sufficient to give a useful theory of molecular motion of an ideal gas? The assumptions that are central to kinetic molecular theory are:

1. Molecules in a gas are in constant, random, rapid motion.
2. The motion is isotropic, meaning the same in all directions.
3. Gas molecules are modeled as point masses, having no volume.
4. No forces act between the molecules, except at the instant of a collision.
5. All collisions are instantaneous and elastic. No energy is lost to other degrees of freedom, such as rotations or vibrations.

The assumption of the negligible volume of the gas molecules is relaxed when considering intermolecular collisions.

The pressure of a gas is the average force of collisions imparted to the walls of a container per unit area:

$$P = \frac{f}{A} \qquad 31.1.1$$

The force of collisions with the wall of a container in a given time interval is given by:

$$f = (\text{number of collisions})(\text{force per collision})(\text{fraction molecules moving in correct direction}) \quad 31.1.2$$

Consider a container with N molecules and volume V , Figure 31.1.1a. The number density of molecules is N/V and the number of moles of gas is $n = N/N_A$, where N_A is Avogadro's number. Consider a portion of the wall in the y - z plane with area A . Each molecule has velocity components v_x , v_y , and v_z , Figure 31.1.1b. However, the rate of collisions with the wall depends only on the x -component of the velocity. Consider one molecule with velocity component $+v_x$. In a given time Δt , the molecule will collide with the wall if the distance between the molecule and the wall is less than or equal to $v_x\Delta t$. The total number of collisions within the area A in time interval Δt is given by the number of molecules in the box with end area A and length $v_x\Delta t$.

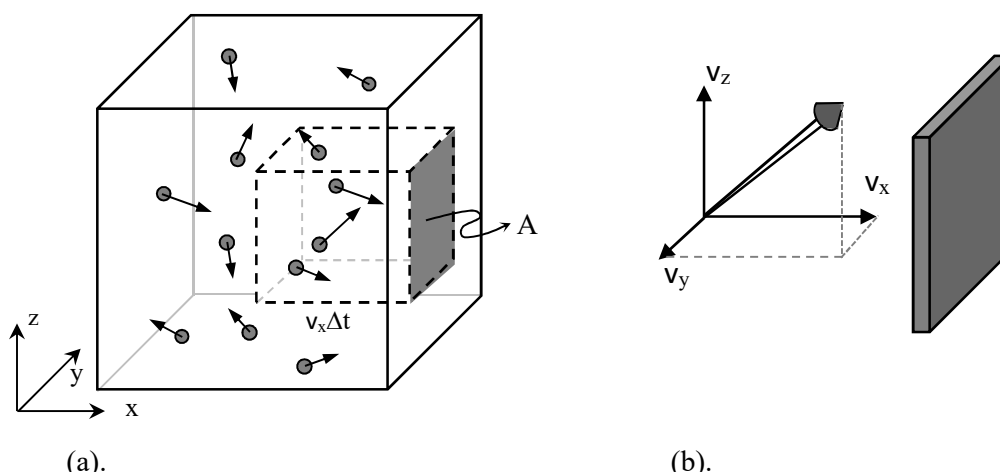


Figure 31.1.1: (a). Molecules within a distance $v_x\Delta t$ strike the wall in the given time interval. Consider the chosen molecule in black. (b). Only the velocity component towards the wall, $+v_x$, determines if a collision occurs.

We needn't worry about the y - and z -components of the molecules in the box. On average, a molecule leaving the box in the y - or z -directions will be replaced by molecule entering the box, Figure 31.1.2a. The number of collision in the time interval Δt is given by the number density and the box volume $Av_x\Delta t$:

$$\text{collisions} = \frac{N}{V} Av_x\Delta t \quad 31.1.3$$

The force of the collision is given by $f = ma = m (dv/dt)$, where m is the mass of the molecule. For a finite time interval with a single collision the force is $f = m (\Delta v_x/\Delta t)$. A molecule initially with velocity $+v_x$ reverses direction after the collision resulting in velocity $-v_x$, giving the change in velocity as $\Delta v_x = (+v_x) - (-v_x) = 2v_x$, Figure 31.1.2b. The force per collision is:

$$\text{force per collision} = \frac{2mv_x}{\Delta t} \quad 31.1.4$$

The total force is the product of the number of collisions in time interval Δt and the force per collision:

$$f = \frac{N}{V} Av_x \Delta t \frac{2mv_x}{\Delta t} = \frac{2NAmv_x^2}{V} \quad 31.1.5$$

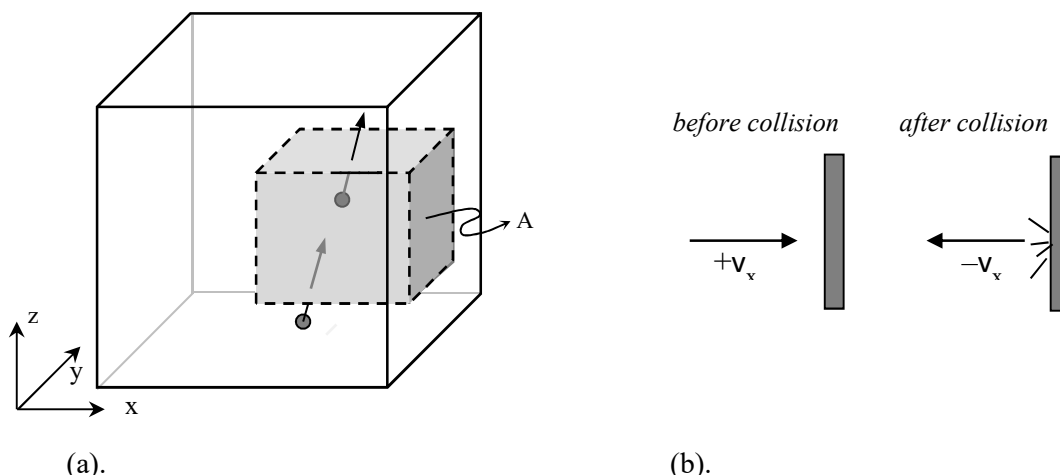


Figure 31.1.2: (a). On average, molecules leaving the box in the y- and z-directions are replaced by molecules entering the box. (b). The change in velocity during the collision is $2v_x$.

Dividing this last equation by the cross-sectional area gives:

$$\frac{f}{A} = \frac{2Nm v_x^2}{V} \quad 31.1.6$$

This relationship assumes the velocity is the single value v_x . Molecules travel with a wide range of velocities, so that the force per unit area must be averaged over all the possible molecular velocities to give the pressure:

$$\frac{\bar{f}}{A} = \frac{2Nm \overline{v_x^2}}{V} \quad 31.1.7$$

We indicate an average with an “over-bar,” where $\overline{v_x^2}$ is the average of the squared velocity. We now determine the number of molecules moving in the correct direction. Only molecules with positive velocities in the x-direction strike the target area. On average half of the molecules are moving in the $+v_x$ direction and half in the $-v_x$ direction. Dividing the last expression by two gives the pressure as:

$$P = \frac{Nm \overline{v_x^2}}{V} \quad 31.1.8$$

In general, we don't need to know the x-, y-, z-components of the velocity. Rather only the magnitude of the velocity is of interest. The speed of a molecule, c , is the magnitude of the velocity, which is related to the x, y, z-components by the Pythagorean theorem:

$$c^2 = v_x^2 + v_y^2 + v_z^2 \quad 31.1.9$$

The average squared speed is then given by:

$$\overline{c^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \quad 31.1.10$$

The motion of the molecules is isotropic, so that the components of the squared velocity on average are equal, $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$. The average squared velocity in the x-direction is then one-third the average squared speed:

$$\overline{c^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2} \quad \text{giving} \quad \overline{v_x^2} = \overline{c^2}/3 \quad 31.1.11$$

Substituting this last expression into Eq. 31.1.8 gives the final result for the pressure:

$$P = \frac{Nm\overline{c^2}}{3V} \quad 31.1.12$$

Note that the average in this last relationship is of the squared speed, which is not equal to the square of the average speed: $\overline{c^2} \neq (\overline{c})^2$. The **root-mean-squared speed**, or **rms-speed**, is defined as:

$$u \equiv (\overline{c^2})^{1/2} \quad 31.1.13$$

Noting that $u^2 = \overline{c^2}$ allows us to write Eq. 31.1.12 in terms of the rms-speed:

$$P = \frac{Nmu^2}{3V} \quad 31.1.14$$

The average translational kinetic energy of a molecule is $\overline{\epsilon_t} = \frac{1}{2} mu^2$. Also note that Eq. 31.1.14 resembles the ideal gas law; multiplying both sides by V gives:

$$PV = \frac{1}{3} N mu^2 = \frac{2}{3} N \overline{\epsilon_t} \quad 31.1.15$$

From the ideal gas law, we also know that $PV = nRT$. The constant R is the gas constant per mole. **Boltzmann's constant** is defined as the gas constant per molecule, $k \equiv R/N_A = 1.38065 \times 10^{-23} \text{ J K}^{-1}$. On a per molecule basis for N molecules, $nR = (N/N_A)(N_A k) = Nk$. Using $PV = NkT$ with Eq. 31.1.15 and solving for the average translational kinetic energy gives:

$$\overline{\epsilon_t} = \frac{3}{2} kT \quad 31.1.16$$

where kT is the available thermal kinetic energy at temperature T per molecule and RT is the available thermal kinetic energy per mole. This result is surprising, since we find that the average translational kinetic energy of an ideal gas is independent of the molar mass. Translational kinetic energy is only a function of temperature. At a given temperature all ideal gases have the same kinetic energy. On a molar basis, $\overline{\epsilon_t} = \frac{3}{2} N_A kT = \frac{3}{2} RT$, as expected from the experimental internal energies of monatomic gases, which only have translational energy. Eq. 31.1.16 is also

expected based on the Equipartition Theorem. Given that $\bar{\epsilon}_t = \frac{1}{2} m u^2$, Eq. 31.1.16 also allows us to find the rms-speed of the molecules as:

$$u = \sqrt{\frac{3 kT}{m}} \quad (\text{m in kg}) \quad 31.1.17$$

The units of the molecular mass in this last equation are kg. Given that the molar mass is $\mathcal{M} = (N_A m)$ and that $N_A k = R$, Eq. 31.1.17 is also written as:

$$u = \sqrt{\frac{3 RT}{\mathcal{M}}} \quad (\mathcal{M} \text{ in kg mol}^{-1}) \quad 31.1.18$$

The rms-speed of the molecules depends on the temperature and the molar mass. At a given temperature heavy molecules move slowly and light molecules move rapidly.

Example 31.1.1: Average Kinetic Energy and rms-Speed

Calculate the average translational kinetic energy and rms-speed of N_2 and CO_2 at 298.2 K.

Answer: The average translational kinetic energy is the same for N_2 and CO_2 . Using Eq. 31.1.16 on a per molecule basis:

$$\bar{\epsilon}_t = \frac{3}{2} kT = \frac{3}{2} (1.38065 \times 10^{-23} \text{ J K}^{-1})(298.2 \text{ K}) = 6.176 \times 10^{-21} \text{ J}$$

On a per mole basis: $\bar{\epsilon}_t = \frac{3}{2} RT = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.2 \text{ K})(1 \text{ kJ}/1000 \text{ J}) = 3.718 \text{ kJ mol}^{-1}$
The rms-speed of the molecules, using Eq. 31.1.18 is:

$$u = \sqrt{\frac{3 RT}{\mathcal{M}}} = \sqrt{\frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{28.013 \text{ g mol}^{-1}(1 \text{ kg}/1000 \text{ g})}} = 515.2 \text{ m s}^{-1} \quad \text{for } N_2$$

$$u = \sqrt{\frac{3(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{44.0098 \text{ g mol}^{-1}(1 \text{ kg}/1000 \text{ g})}} = 411.1 \text{ m s}^{-1} \quad \text{for } CO_2$$

31.2 The Maxwell Distribution

The distribution of molecular speeds is a specific example of a probability distribution. We begin with an instructive example of the determination of average values using a probability distribution. Consider first an experiment that has results given by integers, x_i . There are two basic ways of determining an average. The first is to simply add the results of each trial and divide by the total number of trials, N : $\bar{x} = (1/N) \sum x_i$, Figure 31.2.1. The sum extends over each observation, $i = 1$ to N . The second method is to count the number of occurrences, n_i , of each result x_i . The average is the weighted average with the weighting factors n_i/N :

$$\bar{x} = (1/N) \sum n_i x_i \quad \text{with } N = \sum n_i \quad 31.2.1$$

In this case the sum extends over all possible outcomes of the experiment. The weighting factors are the probabilities of occurrence of each experimental result, $p_i = n_i/N$. This set of probabilities is the **probability distribution** of the outcomes of the experiment, Figure 31.2.1a:

$$\bar{x} = \sum x_i p_i \quad \text{with } p_i = n_i/N \quad \text{and } \sum p_i = 1 \quad 31.2.2$$

Probability distributions should be normalized, $\sum p_i = 1$, giving that the total probability of occurrence of any possible value is one, or 100%. A plot of the probability distribution versus the corresponding experimental value provides a visual summary of the variability in the results, Figure 31.2.1b. The maximum of the probability distribution gives the most probable result, x_{mp} .

- Example data set with $N = 9$ trials:

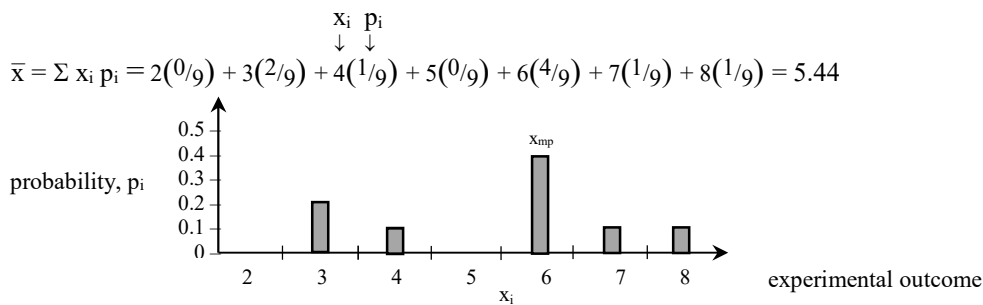
$$x_i: 6 \ 3 \ 4 \ 6 \ 6 \ 3 \ 7 \ 8 \ 6 \quad \text{with } \bar{x} = (1/N) \sum x_i = 49/9 = 5.44$$

- Using a weighted average: each possible result is weighted by the number of occurrences, n_i :

$$\bar{x} = \frac{\sum n_i x_i}{\sum n_i} = \frac{\begin{array}{c} n_i \ x_i \\ \downarrow \downarrow \\ 0(2) + 2(3) + 1(4) + 0(5) + 4(6) + 1(7) + 1(8) \end{array}}{0 + 2 + 1 + 0 + 4 + 1 + 1} = 49/9 = 5.44$$

- Using a probability distribution: the number of occurrences is converted to a probability, $p_i = n_i/N$:

$$(a). \quad \bar{x} = \sum x_i p_i = 2(0/9) + 3(2/9) + 4(1/9) + 5(0/9) + 6(4/9) + 7(1/9) + 8(1/9) = 5.44$$



(b).

Figure 31.2.1: (a). There are two ways of doing averages, the traditional $\bar{x} = (1/N) \sum x_i$ and using a weighted average with the weights given by a probability distribution. (b). The maximum of the probability distribution is the most probable experimental outcome, x_{mp} .

Our example used integer values. If the experimental results are on a continuous range, the summation is replaced by an integral over all possible values of x . Then the probability distribution $p(x) dx$ determines the probability of occurrence of a value in the range of x to $x + dx$. The specification of a range is necessary because the probability of occurrence of any specific exact value, say 6.0111343561, is vanishingly small. But values near 6.00 ± 0.02 may be quite common. The normalization is established by setting the integral over all possible values equal to one:

$$\int_{-\infty}^{\infty} p(x) dx = 1 \quad \text{(normalization)} \quad 31.2.3$$

The average value of x is then given as an integral over the probability distribution. Any function, such as x^2 , may be averaged in an analogous fashion:

$$\bar{x} = \int_{-\infty}^{\infty} x p(x) dx \quad \text{and} \quad \overline{x^2} = \int_{-\infty}^{\infty} x^2 p(x) dx \quad 31.2.4$$

\uparrow \uparrow \uparrow \uparrow
variable to be averaged *variable to be averaged*

If you have studied quantum mechanics, you will notice the parallel with expectation values, for which the probability distribution is $\Psi^2 dx$. Now that we know about probability distributions, we are ready to find the distribution of molecular speeds in an ideal gas.

The Distribution of Molecular Speeds from the Boltzmann Distribution: The distribution of translational kinetic energies can be determined using the particle in a box model from quantum mechanics. If you haven't covered that material yet, don't worry. We will simply present the result, which you can verify during your later study. The result is the Boltzmann distribution for translational energy in one-dimension. Consider a molecule of mass m traveling in the x -direction in a container of length a . The normalization is given by the partition function (see Sec. 8.10 for further information on the Boltzmann distribution and partition functions):

$$q_t = (2\pi mkT)^{1/2} a/h \quad (\text{quantum})(30.2.17^\circ) \quad 31.2.5$$

The distribution function, which is the probability that a particle will have translational kinetic energy ϵ_x , is:

$$p_i = \frac{n_i}{N} = \frac{e^{-\epsilon_x/kT}}{q_t} = \frac{e^{-\epsilon_x/kT}}{(2\pi mkT)^{1/2} a/h} \quad (\text{quantum}) \quad 31.2.6$$

for n_i molecules in energy level i and N total molecules. Classically the kinetic energy in the x -direction is given by $\epsilon_x = \frac{1}{2} mv_x^2$. Noting the exponential form of Eq. 31.2.6 suggests that the classical distribution function of molecular velocities has the form:

$$p(v_x) dv_x = \mathcal{A} e^{-mv_x^2/2kT} dv_x \quad 31.2.7$$

where \mathcal{A} is a normalization constant. (We will do a careful derivation of this functional form in Sec 31.6.) To find the normalization constant, we set the integral over all possible values equal to one:

$$\int_{-\infty}^{\infty} p(v_x) dv_x = \mathcal{A} \int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = 1 \quad 31.2.8$$

Standard tables give the integral as $\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2}$. Substitution into Eq. 31.2.8 results in:

$$\int_{-\infty}^{\infty} p(v_x) dv_x = \mathcal{A} \left(\frac{\pi}{m/2kT}\right)^{1/2} = 1 \quad \text{giving} \quad \mathcal{A} = \left(\frac{m}{2\pi kT}\right)^{1/2} \quad 31.2.9$$

Notice the similarity of the classical normalization with the quantum mechanical partition function and normalization, Eqs. 30.2.17° and 31.2.5. Substitution of the normalization constant back into Eq. 31.2.7 gives the one-dimensional distribution function of molecular velocities as:

$$p(v_x) dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x \quad 31.2.10$$

Analogous relationships hold for motion in the y-, and z-directions. The distribution of velocities is in the general form of a Gaussian distribution, see *General Pattern* **ϕ5** in Chapter 6. A Gaussian distribution with standard deviation of σ and zero mean is:

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2} \quad \text{comparing Eq. 31.2.10 gives: } \sigma = \sqrt{\frac{kT}{m}} \quad 31.2.11$$

A Gaussian distribution has a full-width at half maximum of: $fw\text{hm} = 2\sqrt{2 \ln 2} \sigma = 2.355 \sigma$. Comparing the general form of the Gaussian distribution to Eq. 31.2.10, the standard deviation of the x-velocity is $\sigma_x = \sqrt{kT/m}$. The distribution broadens as the temperature increases.

The kinetic energies of the molecule in the x-, y-, and z-directions are independent. The molecule can have any values for the three components without restriction. As a result for a three-dimensional container the total kinetic energy is the sum: $\epsilon_t = \frac{1}{2} m(v_x^2 + v_y^2 + v_z^2)$ and the overall distribution function is the product of the one-dimensional distribution functions in x, y, and z:

$$p(v_x, v_y, v_z) dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} dv_x dv_y dv_z \quad 31.2.12$$

The result is the probability of a molecule having velocities in the ranges $[v_x, v_x + dv_x]$, $[v_y, v_y + dv_y]$, and $[v_z, v_z + dv_z]$. However, that is way too much information. We usually don't care about the individual components of the velocity. Rather, we only need to know the speed of the molecule, independent of the direction of travel. As we did in Eq. 31.1.11, the squared speed and corresponding total translational kinetic energy are related to the velocity components by:

$$c^2 = v_x^2 + v_y^2 + v_z^2 \quad \text{and} \quad \epsilon_t = \frac{1}{2} mc^2 \quad 31.2.13$$

Substituting these two relationships into Eq. 31.2.12, the distribution function of the speed is:

$$p(c) dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} dv_x dv_y dv_z \quad 31.2.14$$

The differentials are still in an awkward form. Because the motion of a molecule in a gas is isotropic, this equation is simplified by conversion to spherical polar coordinates. We need to take a short diversion to discuss spherical polar coordinates and averaging in three-dimensions.

Spherical Polar Coordinates Simplify Spherically Symmetrical Systems: For an isotropic system, the spherical polar coordinate system is useful for determining the velocity of a molecule. The speed of the molecule, c , is the length of the velocity vector, Figure 31.2.2. The polar angle, θ , is the angle between the z-axis and the vector. The azimuthal angle, ϕ , is the angle between the x-axis and the projection of the vector onto the xy-plane. To completely cover all space, the ranges of the coordinates are:

$$0 \leq c \leq \infty \quad 0 \leq \theta \leq \pi \quad 0 \leq \phi \leq 2\pi \quad 31.2.15$$

The projection of the vector onto the z-axis is $c \cos \theta$, Figure 31.2.3a. The projection of the vector onto the xy-plane has length $c \sin \theta$. The transformation between spherical polar coordinates and Cartesian coordinates is then given by Eq. 31.2.13 and:

$$c = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

$$v_x = c \sin \theta \cos \phi$$

$$v_y = c \sin \theta \sin \phi$$

$$v_z = c \cos \theta$$

31.2.16

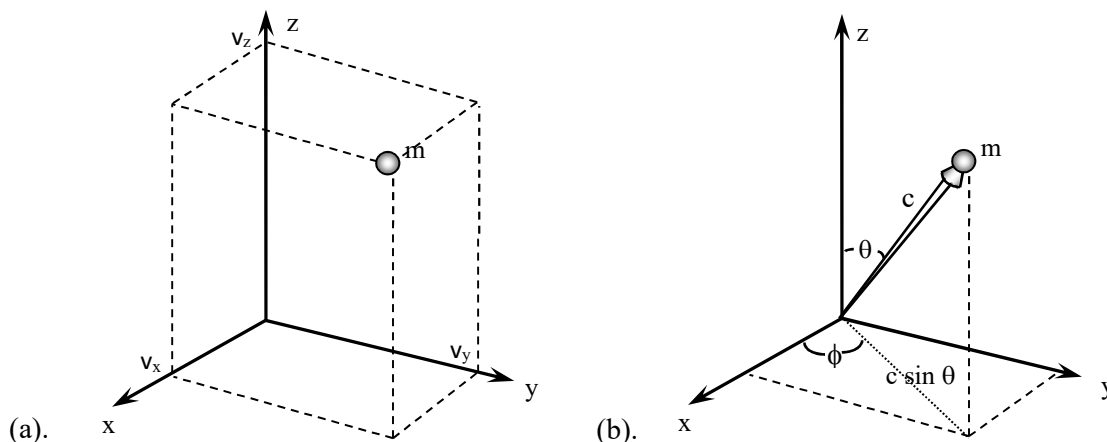


Figure 31.2.2: (a). A molecule of mass m with velocity components v_x , v_y , v_z . (b). Spherical polar coordinates, c , θ , and ϕ completely specify the position of the particle.

Spherical polar coordinates are particularly useful for simplifying integrals in spherically symmetric systems. For example consider the integral of a function $f(v_x, v_y, v_z)$ in Cartesian coordinates over all velocities:

$$I = \int_0^\infty \int_0^\infty \int_0^\infty f(v_x, v_y, v_z) dv_x dv_y dv_z \quad 31.2.17$$

In general terms the differential is called the **volume element**, which is given the symbol $d\tau$. In Eq. 31.2.17 the volume element of Cartesian velocities is $d\tau = dv_x dv_y dv_z$. The volume element is the volume of an infinitesimal “box” of sides lengths dv_x , dv_y , and dv_z that is swept out by a change from v_x to $v_x + dv_x$, from v_y to $v_y + dv_y$, and from v_z to $v_z + dv_z$, respectively. What is the corresponding volume element in spherical polar coordinates?

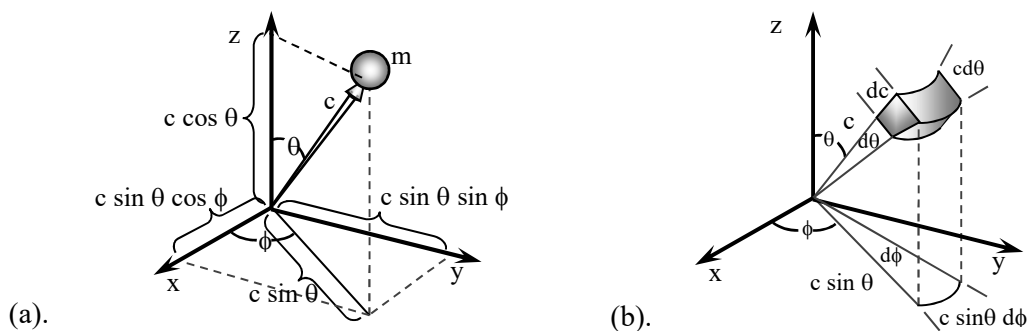


Figure 31.2.3: (a). The transformation from r , θ , ϕ to x , y , z . (b). The volume element in “three-space” in spherical polar coordinates: $d\tau = c^2 \sin \theta dc d\theta d\phi$.

Consider a change in c , θ , and ϕ from c to $c + dc$, θ to $\theta + d\theta$, and ϕ to $\phi + d\phi$. The corresponding sides of the small volume element that are swept out by these differential changes are dc , $c d\theta$, and $c \sin \theta d\phi$, Figure 24.5.3b. The volume element in three-space is the product of these sides:

$$d\tau = dv_x dv_y dv_z = dc (c d\theta)(c \sin \theta d\phi) = c^2 \sin \theta dc d\theta d\phi \quad 31.2.18$$

In spherical polar coordinates, the integral in Eq. 31.2.17 is written:

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} f(c, \theta, \phi) c^2 \sin \theta dc d\theta d\phi \quad 31.2.19$$

Quite commonly, the function to be integrated only depends on the speed, $f(c)$, and is independent of orientation. The integral is then **separable**, the integral factors into a product of three one-dimensional integrals:

$$I = \int_0^\infty f(c) c^2 dc \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \quad 31.2.20$$

The integrals over all possible θ values and over all possible ϕ values are:

$$\int_0^\pi \sin \theta d\theta = [-\cos \theta]_0^\pi = 1 + 1 = 2 \quad \text{and} \quad \int_0^{2\pi} d\phi = [\phi]_0^{2\pi} = 2\pi \quad 31.2.21$$

The angular portion of the integral over all space is then just 4π :

$$\int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\phi = 4\pi \quad 31.2.22$$

Given a spherically symmetrical function $f(c)$, Eq. 31.2.20 then simplifies to:

$$I = 4\pi \int_0^\infty f(c) c^2 dc \quad 31.2.23$$

The factor of $4\pi c^2 dc$ is the volume of an annular region with radius c and thickness dc , Figure 31.2.3a. The volume of the annular region increases as c^2 . In other words, for the same thickness, there are many more increments of volume at large c compared to small c , Figure 31.2.3b. Please see Sec. 24.5 and Addendum 24.8.1 for additional information on integration in multiple dimensions.

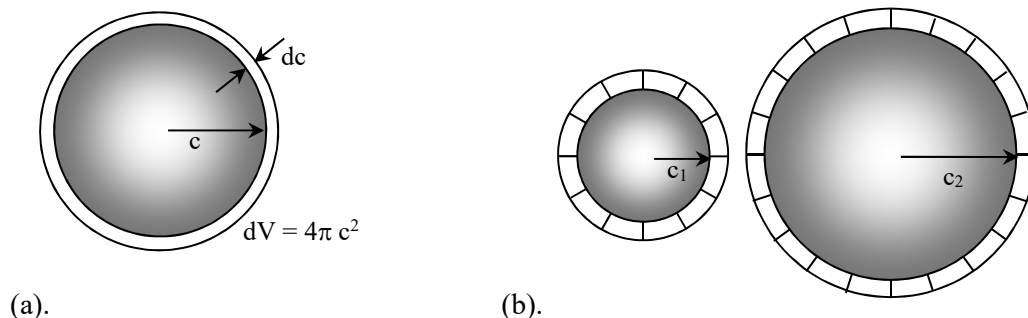


Figure 31.2.3: (a). The volume of an annular region of thickness dc is $dV = 4\pi c^2 dc$. A thin annular region is like a thin spherical piece of onion skin. (b). For the same thickness, a small increase in radius gives a large increase in annular volume. The segments are equal in volume for the two cases shown.

Averaging in 3-Dimensions: For an average of the function f in three dimensions, the probability distribution can be expressed in terms of Cartesian, $p(v_x, v_y, v_z)$, or spherical polar coordinates, $p(c, \theta, \phi)$. Eqs. 31.2.16 are used to transform $p(v_x, v_y, v_z)$ to $p(c, \theta, \phi)$ and $f(v_x, v_y, v_z)$ to $f(c, \theta, \phi)$. The average of a function f is given equivalently in Cartesian and spherical polar coordinates by:

$$\begin{aligned}\bar{f} &= \int_0^\infty \int_0^\infty \int_0^\infty f(v_x, v_y, v_z) p(v_x, v_y, v_z) dv_x dv_y dv_z \\ \bar{f} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} f(c, \theta, \phi) p(c, \theta, \phi) c^2 \sin \theta dc d\theta d\phi\end{aligned}\quad 31.2.24$$

For our case, we wish to find the averages of the speed, squared speed, and kinetic energy, none of which depends on angles θ and ϕ . Spherical polar coordinates simplify the integrals using Eqs. 31.2.22 and 31.2.23.

The Maxwell Distribution of Molecular Speeds has a Maximum: We don't need to know the direction of motion. Converting Eq. 31.2.14 to spherical polar coordinates and averaging over the direction of the motion gives the distribution function of molecular speeds as:

$$p(c) dc = \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\pi \int_0^{2\pi} e^{-mc^2/2kT} c^2 \sin\theta dc d\theta d\phi \quad 31.2.25$$

The integral is separable. The angular integrals then reduce to 4π , Eq. 31.2.23. The result is the **Maxwell distribution of molecular speeds**:

$$p(c) dc = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2 dc \quad 31.2.26$$

A plot of the Maxwell distribution for O_2 at several temperatures shows that as the temperature increases the distribution broadens and the most probable speed increases, Figure 31.2.4. As the distribution broadens, the maximum value of the probability decreases to maintain normalization; the area under the curve must remain at unity and the distribution "flattens." As temperature increases, the probability of molecules with high speed, while small, increases greatly. This increase in energy rich molecules is the reason that organic and inorganic chemists often heat their flasks during synthetic reactions. The importance of the Maxwell distribution to chemical kinetics is difficult to overstate.

The Maxwell distribution is the product of a decreasing function and an increasing function of speed. The decreasing function is the exponential term $e^{-mc^2/2kT}$. The probability of high kinetic energies is less than low kinetic energies for a specific speed and direction, as specified by c , θ , and ϕ . The increasing function is the volume of the annular region, which is $4\pi c^2 dc$. As the speed increases there is more volume for possible values at the given speed, independent of direction, Figure 31.2.3b. The product of a decreasing function and an increasing function has a maximum value. Very slow speeds and very high speeds are improbable. The most-probable speed, c_{mp} , is given by setting the derivative of the Maxwell distribution with respect to speed equal to zero (see the Problems):

$$\frac{dp}{dc} = 0 \quad \text{giving} \quad c_{mp} = \sqrt{\frac{2kT}{m}} \quad 31.2.27$$

With the Maxwell relationship in hand, we next determine the average speed of the molecules in an ideal gas.

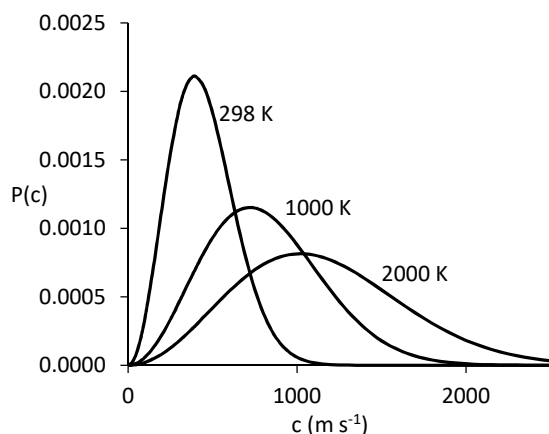


Figure 31.2.4: Maxwell distribution of molecular speeds at increasing temperatures. Few molecules have low speeds and few have high speeds.

The Average Speed is Less than the RMS-Speed: The average speed of a molecule at temperature T is given by the integral over the Maxwell distribution:

$$\bar{c} = \int_0^{\infty} c p(c) dc \quad 31.2.28$$

Using the Maxwell distribution, Eq. 31.2.26, the integral becomes:

$$\bar{c} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} c^3 e^{-mc^2/2kT} dc \quad 31.2.29$$

Standard tables give the integral as $\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2}$, which upon substitution gives:

$$\bar{c} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m} \right)^2 = \frac{2}{\pi^{1/2}} \left(\frac{m}{2kT} \right)^{-1/2} \quad 31.2.30$$

Gathering the constants gives the average speed:

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi \mathcal{M}}} \quad (\mathcal{M} \text{ in kg mol}^{-1}) \quad 31.2.31$$

Notice that the average of c ends up being an integral over c^3 , which results from the product of c with the volume element $4\pi c^2 dc$.

The average squared speed of a molecule at temperature T is given by the integral over the Maxwell distribution:

$$\overline{c^2} = \int_0^{\infty} c^2 p(c) dc \quad 31.2.32$$

Using the Maxwell distribution, Eq. 31.2.26, the integral becomes:

$$\overline{c^2} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty c^4 e^{-mc^2/2kT} dc \quad 31.2.33$$

Standard tables give the integral as $\int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{8a^2} \left(\frac{\pi}{a} \right)^{1/2}$, which upon substitution gives:

$$\overline{c^2} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \frac{3}{8} \left(\frac{2kT}{m} \right)^2 \left(\frac{2\pi kT}{m} \right)^{1/2} = \frac{4 \cdot 3}{8} \left(\frac{\pi \cdot \pi^{1/2}}{\pi^{3/2}} \right) \left(\frac{m}{2kT} \right)^{3/2} \left(\frac{2kT}{m} \right)^{5/2} = \frac{3kT}{m} \quad 31.2.34$$

Taking the square root gives the rms-speed as:

$$u = (\overline{c^2})^{1/2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{\mathcal{M}}} \quad (\mathcal{M} \text{ in kg mol}^{-1}) \quad 31.2.35$$

We derived this same expression as Eq. 31.1.17, based on the ideal gas law. Our current derivation is from first principles and avoids using the empirical gas law. We should compare the various measures of molecular speed that we have derived in Eqs. 31.2.27, 31.2.31, and 31.2.35. For the average speed, \bar{c} , the numerical constant is $8/\pi = 2.546$, which shows that $c_{mp} < \bar{c} < u$, Figure 31.2.5. The reason for the differences is that the averages in \bar{c} and u include large values of c , which while improbable do increase the averages slightly compared to the most probable value. Because of the c^2 -dependence in $u = (\overline{c^2})^{1/2}$, the rms-speed weights the fast speeds from the “tail” of the Maxwell distribution more heavily than the average speed.

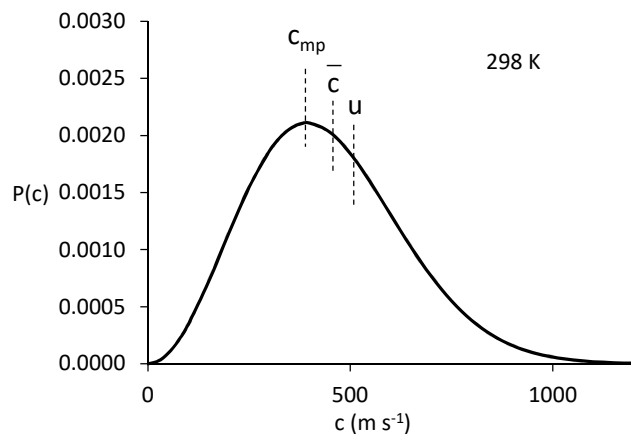


Figure 31.2.5: Comparison of the most probable, average, and rms-speeds of O_2 at 298.2 K, which are $c_{mp} = 394 \text{ m s}^{-1}$, $\bar{c} = 444 \text{ m s}^{-1}$, and $u = (\overline{c^2})^{1/2} = 482 \text{ m s}^{-1}$.

31.3 The Rate of Molecular Collisions

Collisions with a Wall: Effusion: Collisions with the walls of a reaction vessel, the surfaces of solid particles, or solid substrates can accelerate or decelerate chemical reactions. The same general theory also applies to gas phase effusion, which is used in isotope separation, the measurement of vapor pressure of solids, and the determination of molecular masses. Collisions of molecules with a wall closely parallels our derivation of the pressure of a gas.

Once again consider a container with N molecules and volume V , Figure 31.1.1a, The number density of molecules is N/V and the mass density is $d = n \mathcal{M}/V$, where \mathcal{M} is the molar mass of the molecules. Consider a portion of the wall in the y - z plane with area A . Consider one molecule with velocity component $+v_x$. In a given time Δt , the molecule will collide with the wall if the distance between the molecule and the wall is less than or equal to $v_x \Delta t$. The total number of collisions within the area A in time interval Δt is given by the number of molecules in the box with end area A and length $v_x \Delta t$, Eq. 31.1.3. The rate of collisions per unit area is given by dividing by $A \Delta t$:

$$\text{collision rate per unit area} = \frac{N}{V} v_x \quad 31.3.1$$

We only considered one velocity. The collision rate is determined by averaging over the distribution of velocities in the positive x -direction. Only molecules with velocity $+v_x$ are headed towards the wall. Using the velocity distribution in Eq. 31.2.10, the average collision rate per unit area, Z_{wall} , is:

$$Z_{\text{wall}} = \frac{N}{V} \int_0^{\infty} v_x p(v_x) dv_x = \frac{N}{V} \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^{\infty} v_x e^{-mv_x^2/2kT} dv_x \quad 31.3.2$$

Standard tables give the integral as $\int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a}$, which upon substitution gives:

$$Z_{\text{wall}} = \frac{N}{V} \left(\frac{m}{2\pi kT} \right)^{1/2} \left(\frac{2kT}{2m} \right) = \frac{N}{V} \left(\frac{kT}{2\pi m} \right)^{1/2} \quad 31.3.3$$

This expression can be rewritten in terms of the average speed, Eq. 31.2.31. Multiplying and dividing by 4, rearranging, and substituting the relationship for the average speed gives the average collision rate per unit area as:

$$Z_{\text{wall}} = \frac{1}{4} \frac{N}{V} \left(\frac{8kT}{\pi m} \right)^{1/2} = \frac{1}{4} \frac{N}{V} \left(\frac{8RT}{\pi \mathcal{M}} \right)^{1/2} = \frac{1}{4} \frac{N}{V} \bar{c} \quad (\mathcal{M} \text{ in kg mol}^{-1}) \quad 31.3.4$$

As the average speed of the molecules increases, the collisions with the walls of the container increase. The average speed increases with temperature as $T^{1/2}$ and decreases with molar mass as $\mathcal{M}^{-1/2}$. The dependence on molar mass is the key to practical applications.

In gas **effusion**, a gas is placed in a container with a small hole. “Collisions” with the hole allow molecules to escape from the container. The rate of escape is the **effusion rate**. If the wall surrounding the hole is so thin that the escaping molecules don’t collide with the side-wall of the hole, then the effusion rate is given by Eq. 31.3.3 multiplied by the cross-sectional area of the hole:

$$\text{effusion rate} = \frac{dN}{dt} = Z_{\text{wall}} A = \frac{N}{V} A \left(\frac{RT}{2\pi \mathcal{M}} \right)^{1/2} \quad 31.3.5$$

where N is the number of molecules of gas escaping the container. The number density is given by the ideal gas law as $N/V = N_A P/RT$. The effusion rate in moles of molecules per second, dn/dt , is then given by dividing Eq. 31.3.5 by Avogadro’s number:

$$\text{effusion rate} = \frac{dn}{dt} = \frac{Z_{\text{wall}} A}{N_A} = \frac{P}{RT} A \left(\frac{RT}{2\pi \mathcal{M}} \right)^{1/2} = P A \left(\frac{1}{2\pi \mathcal{M} RT} \right)^{1/2} \quad 31.3.6$$

For mixtures of gases, P is replaced by the partial pressure of the substance, P_i . Consider a mixture of two types of molecules with molar masses \mathcal{M}_1 and \mathcal{M}_2 . The ratio of the rates of effusion of n_1 moles of molecules of type 1 and n_2 moles of molecules of type 2 using Eq. 31.3.5 for each substance or Eq. 31.3.6 for each substance is:

$$\frac{\text{effusion rate 2}}{\text{effusion rate 1}} = \frac{n_2}{n_1} \left(\frac{\mathcal{M}_1}{\mathcal{M}_2} \right)^{1/2} = \frac{P_2}{P_1} \left(\frac{\mathcal{M}_1}{\mathcal{M}_2} \right)^{1/2} \quad 31.3.7$$

Effusion and processes related to effusion are used to separate uranium isotopes based on the gases $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ and the small difference in molar mass. The dependence on pressure also allows effusion to be used to measure the vapor pressures of solids.

The Rate of Molecular Collisions in Ambient Conditions is Screamingly Fast: The collision rate in gases near ambient conditions is amazingly fast. The **hard-core collision** model for collisions between A and B molecules assumes that the molecules have volume, but no forces act between the molecules except at the instant of a collision. We model each molecule, no matter how complex, as a sphere with radius r_A for A and r_B for B. The molecules act like billiard balls during the collisions. Consider N_A molecules of A and N_B molecules of B in a container of volume V . The number density of A molecules is N_A/V and of B molecules is N_B/V . The centers of mass of A and B must approach each other to a distance of $d = r_A + r_B$ for a collision to occur, Figure 31.3.1. The parameter d is the **hard-core collision diameter**. Any B molecule approaching A within the **hard-core collision cross section**, σ_{HC} , undergoes a collision, with σ_{HC} given as the area of the circle with radius d :

$$\sigma_{\text{HC}} = \pi (r_A + r_B)^2 = \pi d^2 \quad 31.3.8$$

To simplify matters, we initially assume that molecule A is moving with average speed \bar{c} and all B-molecules are in fixed positions. In time interval Δt , molecule A sweeps out a cylinder of cross-section σ_{HC} and length $\bar{c} \Delta t$, Figure 31.3.1.

$$\text{swept volume} = \sigma_{\text{HC}} \bar{c} \Delta t \quad 31.3.9$$

The molecules travel a zig-zag path caused by the collisions, but the swept volume is the same.

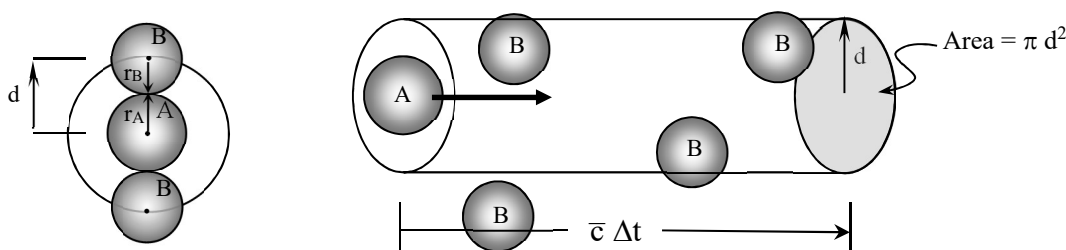


Figure 31.3.1: The hard core collision diameter is the distance of closest approach of molecule A with radius r_A and molecule B with radius r_B : $d = r_A + r_B$. A collision occurs if a B molecule center of mass is in the volume swept by molecule A in time interval Δt .

Any B molecule with a center in this volume undergoes a collision during the time interval. The number of molecules inside this volume is given by the number density of B:

$$\text{number of molecules inside swept volume} = \sigma_{\text{HC}} \bar{c} \Delta t N_{\text{B}}/V \quad 31.3.10$$

The collision frequency is the number of collision per unit time. Dividing the last equation by Δt gives:

$$\text{collision frequency} = \sigma_{\text{HC}} \bar{c} N_{\text{B}}/V \quad 31.3.11$$

We have only considered one A-molecule. Multiplying the last equation by the total number of A-molecules gives the total of collision rate in volume V:

$$\text{collision rate} = N_{\text{A}} \sigma_{\text{HC}} \bar{c} N_{\text{B}}/V \quad 31.3.12$$

Usually we require the collision rate per unit volume. Dividing the last equation by the volume gives:

$$\text{collision rate per unit volume:} = \sigma_{\text{HC}} \bar{c} (N_{\text{A}}/V)(N_{\text{B}}/V) \quad 31.3.13$$

Our model assumes that the B-molecules are not moving, which of course is unrealistic. To relax this restriction, we must replace the average speed of the A-molecules with the average relative speed of the molecules, \bar{c}_{rel} . The speed of approach of A and B molecules relative to each other determines the collision rate. We will show in Sec. 32.5 that the average relative speed has the same form as \bar{c} except that the mass is replaced with the reduced mass of the colliding pair of molecules:

$$\bar{c}_{\text{rel}} = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \quad 31.3.14$$

$$\text{with } \mu = \frac{m_{\text{A}} m_{\text{B}}}{m_{\text{A}} + m_{\text{B}}} = \left(\frac{\mathcal{N}_{\text{A}} \mathcal{N}_{\text{B}}}{\mathcal{N}_{\text{A}} + \mathcal{N}_{\text{B}}} \right) \frac{1}{N_{\text{A}}} (1 \text{ kg}/1000 \text{ g}) \quad 31.3.15$$

Substitution of the relative speed into Eq. 31.3.13 gives the A-B collision rate per unit volume, Z_{AB} :

$$Z_{\text{AB}} = \sigma_{\text{HC}} \bar{c}_{\text{rel}} (N_{\text{A}}/V)(N_{\text{B}}/V) \quad 31.3.16$$

The last equation was derived for bimolecular collisions of dissimilar molecules. In a pure gas or for A-A collisions in a mixture, the collision partners are identical, with $N = N_{\text{A}}$ and $m = m_{\text{A}}$. The reduced mass is $\mu = m/2$ and the relative speed, Eq. 31.3.14, simplifies to:

$$\bar{c}_{\text{rel}} = \left(\frac{8kT}{\pi m/2} \right)^{1/2} = \sqrt{2} \left(\frac{8kT}{\pi m} \right)^{1/2} = \sqrt{2} \bar{c} \quad (\text{A-A}) \quad 31.3.17$$

For A-A collisions the collision rate per unit volume is:

$$Z_{\text{AA}} = \frac{1}{2} \sigma_{\text{HC}} \sqrt{2} \bar{c} (N/V)^2 \quad 31.3.18$$

The leading factor of $\frac{1}{2}$ adjusts for the fact that a collision of molecule 1 with molecule 2 is the same encounter as a collision of molecule 2 with molecule 1.

Example 31.3.1: Hard-Core Collision Rate

Calculate the collision rate per cubic meter in pure O₂ at 1 bar and 298.2 K. Hard-core collision diameters are typically listed in the literature, which are twice the radius of the molecule: $d_{\text{O}_2} = (2 r_{\text{O}_2}) = 3.61 \text{ \AA}$.

Answer: The collision cross-section, using Eq. 31.3.6:

$$\sigma_{\text{HC}} = \pi (2r_{\text{A}})^2 = \pi [3.61 \times 10^{-10} \text{ m}]^2 = 4.094 \times 10^{-19} \text{ m}^2 = 0.409 \text{ nm}^2 = 40.9 \text{ \AA}^2$$

The mass of O₂ is: $m = 32.00 \text{ g mol}^{-1} (1 \text{ kg}/1000 \text{ g})/6.0221 \times 10^{23} \text{ mol}^{-1} = 5.331 \times 10^{-26} \text{ kg}$

With Eq. 31.2.31 the average speed of O₂ molecules at 298.2 K is:

$$\bar{c} = \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1})(298.2 \text{ K})}{\pi 5.331 \times 10^{-26} \text{ kg}} \right)^{1/2} = 443.5 \text{ m s}^{-1}$$

The number density is given by the ideal gas law with 1 bar = $1 \times 10^5 \text{ Pa} = 1 \times 10^5 \text{ N m}^{-2}$ as:

$$N/V = N_{\text{A}}P/RT = \frac{6.0221 \times 10^{23} \text{ mol}^{-1}(1.00 \times 10^5 \text{ N m}^{-2})}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(298.2 \text{ K})} = 2.429 \times 10^{25} \text{ m}^{-3}$$

Concerning the units, remember that 1 J = 1 N m. Using Eq.31.3.18 gives the collision rate per square meter as:

$$\begin{aligned} Z_{\text{AA}} &= \frac{1}{2} \sigma_{\text{HC}} \sqrt{2} \bar{c} (N/V)^2 = \frac{1}{2} 4.094 \times 10^{-19} \text{ m}^2 \sqrt{2} (443.5 \text{ m s}^{-1})(2.429 \times 10^{25} \text{ m}^{-3})^2 \\ &= 7.57 \times 10^{34} \text{ s}^{-1} \text{ m}^{-3} \end{aligned}$$

Since the mass and size of O₂ and N₂ are similar, the total collision rate in ambient air is roughly the same. The large collision rate results from the large number density and rapid movement. Even though the collision cross-section is tiny, 41 Å², the overall collision rate is immense. This result presents the important question: if the collision rate is so screamingly fast, why are gas phase chemical reactions often slow in comparison?

We will take a careful look at relative coordinates in Sec.31.5. However, we can justify that the relative speed is $\sqrt{2}$ times the average speed in the special case of A-A collisions. Picture two bumper cars at your favorite amusement park; obviously the point is to suffer collisions. The best collision occurs if the cars travel in opposite directions on the track. If both cars are traveling at the same speed in the same direction, no collisions occur. The two bumper cars must move at different speeds and/or in different directions. The two cars must have relative motion towards each other. If both cars are traveling in the same direction, but at different speeds, the relative speed is the difference, $c_{\text{rel}} = c_1 - c_2$. If c_1 is 8 km hr⁻¹ and c_2 is 10 km hr⁻¹ the relative speed is -2 km hr⁻¹.

Each molecule has a velocity vector that determines the speed and direction of travel. The velocity vectors for molecules 1 and 2 are \vec{v}_1 and \vec{v}_2 . The relative velocity of the two molecules is the vector difference $\vec{v}_{\text{rel}} = \vec{v}_1 - \vec{v}_2$, Figure 31.3.2a. The relative speed is the length of the relative velocity vector. Consider two molecules moving at the same average speed, \bar{c} . If the molecules travel in opposite directions, the relative speed is $2\bar{c}$, Figure 31.3.2b. If the two

molecules travel in the same direction, the relative speed is zero and they never approach each other, Figure 31.3.2c. In general, collisions occur at all possible angles, from $\theta = 0^\circ$ to 180° . The “average” angle of a collision is 90° , Figure 31.3.2d. The vectors \vec{v}_1 and \vec{v}_2 each have length \bar{c} ; from the Pythagorean theorem the relative speed is $\sqrt{2} \bar{c}$.

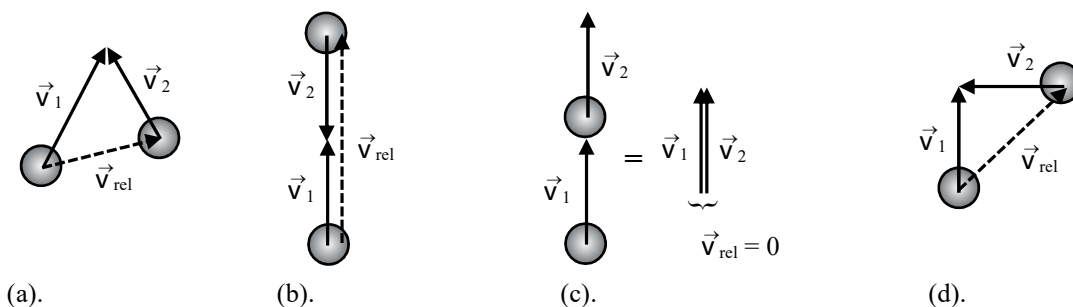


Figure 31.3.2: (a). The relative velocity is $\vec{v}_{\text{rel}} = \vec{v}_1 - \vec{v}_2$ and \bar{c}_{rel} is the length of \vec{v}_{rel} . (b). Assume each molecule travels at the average speed, \bar{c} . If the molecules travel in opposite directions, $\bar{c}_{\text{rel}} = 2\bar{c}$. (c). If both molecules travel in the same direction, $\bar{c}_{\text{rel}} = 0$. (d). For an average collision, at 90° , $\bar{c}_{\text{rel}} = \sqrt{2} \bar{c}$.

Molecules must collide for a chemical reaction to occur: We can use the hard-core collision rate, Z_{AB} , to estimate the rates of chemical reactions. Consider the ideal gas reaction:



If every collision is successful and gives products, the rate of the reaction is given by the rate of collisions:

$$-\frac{d(N_{\text{A}}/V)}{dt} = Z_{\text{AB}} = \sigma_{\text{HC}} \bar{c}_{\text{rel}} \left(\frac{N_{\text{A}}}{V}\right) \left(\frac{N_{\text{B}}}{V}\right) \quad 31.3.20$$

We normally express reaction rate laws in terms of the concentrations of the reactants. The gas-phase concentrations of A and B are given as:

$$[\text{A}] = \frac{1}{N_{\text{A}}} \left(\frac{N_{\text{A}}}{V}\right) \quad \text{and} \quad [\text{B}] = \frac{1}{N_{\text{A}}} \left(\frac{N_{\text{B}}}{V}\right) \quad 31.3.21$$

Dividing both sides of Eq. 31.3.20 by Avogadro’s number, N_{A} , and using $(N_{\text{A}}/V) = N_{\text{A}} (N_{\text{A}}/N_{\text{A}}V)$ converts the number densities to molar concentrations:

$$-\frac{d(N_{\text{A}}/N_{\text{A}}V)}{dt} = \frac{Z_{\text{AB}}}{N_{\text{A}}} = \sigma_{\text{HC}} \bar{c}_{\text{rel}} N_{\text{A}} \left(\frac{N_{\text{A}}}{N_{\text{A}}V}\right) \left(\frac{N_{\text{B}}}{N_{\text{A}}V}\right) \quad 31.3.22$$

Substituting the concentrations from Eq. 31.3.21 into Eq. 31.3.22 gives the reaction rate as:

$$-\frac{d[\text{A}]}{dt} = \frac{Z_{\text{AB}}}{N_{\text{A}}} = \sigma_{\text{HC}} \bar{c}_{\text{rel}} N_{\text{A}} [\text{A}] [\text{B}] \quad 31.3.23$$

The rate law for a second-order elementary mechanistic step has the conventional form:

$$-\frac{d[A]}{dt} = k_2 [A] [B] \quad 31.3.24$$

Comparing Eqs. 31.2.23 and 31.3.24 gives the second-order rate constant, k_2 , as:

$$k_2 = \sigma_{\text{HC}} \bar{c}_{\text{rel}} N_A = \sigma_{\text{HC}} \left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A = \pi d^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} (1000 \text{ L/m}^3) N_A \quad 31.3.25$$

The units of $\sigma_{\text{HC}} \bar{c}_{\text{rel}}$ are $\text{m}^3 \text{s}^{-1}$. To convert k_2 to $\text{L mol}^{-1} \text{s}^{-1}$, we use $1 \text{ m}^3 = 1000 \text{ L}$. Of course not every collision is successful. Kinetic molecular theory offers no method for correcting that assumption. Instead, Eq. 31.3.25 gives the upper limit for the reaction rate.

Example 31.3.2: *Bimolecular Rate Constants and Hard-Core Collision Theory*

Predict the bimolecular rate constant of the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$ at 700.0 K using hard-core collision theory. Assume the hard-core collision radii are: $r_{\text{H}_2} = 1.1 \text{ \AA}$ and $r_{\text{I}_2} = 1.7 \text{ \AA}$.

Answer: The collision cross-section, using Eq. 31.3.6, is:

$$\sigma_{\text{HC}} = \pi (r_A + r_B)^2 = \pi (1.1 \times 10^{-10} \text{ m} + 1.7 \times 10^{-10} \text{ m})^2 = 2.46 \times 10^{-19} \text{ m}^2 = 0.246 \text{ nm}^2 = 24.6 \text{ \AA}^2$$

The reduced mass of the collision is:

$$\begin{aligned} \mu &= \left(\frac{\mathcal{M}_A \mathcal{M}_B}{\mathcal{M}_A + \mathcal{M}_B}\right) \frac{1}{N_A} (1 \text{ kg}/1000 \text{ g}) = \left(\frac{2.02 \text{ g mol}^{-1}(253.81 \text{ g mol}^{-1})}{2.02 \text{ g mol}^{-1} + 253.81 \text{ g mol}^{-1}}\right) \frac{1}{N_A} (1 \text{ kg}/1000 \text{ g}) \\ &= 3.321 \times 10^{-27} \text{ kg} \end{aligned}$$

With Eq. 31.3.14 the relative speed is:

$$\bar{c}_{\text{rel}} = \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1})(700.0 \text{ K})}{\pi 3.321 \times 10^{-27} \text{ kg}}\right)^{1/2} = 2722. \text{ m s}^{-1}$$

Assuming each collision is successful, the rate constant is predicted to be, Eq. 31.3.25:

$$\begin{aligned} k_2 &= \sigma_{\text{HC}} \bar{c}_{\text{rel}} (1000 \text{ L/m}^3) N_A = 2.46 \times 10^{-19} \text{ m}^2 (2722. \text{ m s}^{-1})(1000 \text{ L/m}^3) 6.022 \times 10^{23} \text{ mol}^{-1} \\ &= 4.03 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

This result gives an upper limit to the observed rate constant.

The deficiencies of the hard-core prediction of bimolecular rate constants are significant. The basic theory neglects intermolecular forces. An attractive potential between collision partners increases the effective collision cross-section. The colliding partners don't need to be so close together for an interaction to occur. Molecules also have a softer repulsive potential than assumed in the hard-core model. Molecules aren't spherical structureless particles. Molecular shape, molecular rotation, and vibration are important. Not every collision is successful in bringing about the bond breaking and making steps required for the formation of products. More fundamentally the molecules should be represented by strongly interacting quantum mechanical wave functions. Classical theory cannot provide the detailed description of molecular collisions

that is required for accurate predictions of rate constants. Molecular reactions dynamics is the subject of the next chapter. One important correction is to take the kinetic energy of the collision into account.

Mean Free Path and the Rate of Molecular Collisions: The **mean free path** is the average distance between molecular collisions. The collision rate per unit volume is Z_{AA} . The volume per molecule is the inverse of the number density, V/N . If the molecule is traveling at an average speed of \bar{c} and undergoes collisions at a rate of $(Z_{AA} V/N)$, the mean free path, λ , is defined as:

$$\lambda = \frac{\bar{c}}{Z_{AA} V/N} \quad 31.3.26$$

The units are $(\text{m s}^{-1})/(\text{s}^{-1} \text{m}^{-3} \text{m}^3) = \text{m}$. Using Eq. 31.3.18 for the collision rate and the ideal gas law for the volume per molecule $V/N = (1/N_A)RT/P = kT/P$, Eq. 31.3.26 reduces to:

$$\lambda = \frac{\bar{c}}{\sigma_{\text{HC}} \sqrt{2} \bar{c} (N/V)^2 (V/N)} = \frac{V}{\sqrt{2} \sigma_{\text{HC}} N} = \frac{kT}{\sqrt{2} \sigma_{\text{HC}} P} = \frac{RT}{\sqrt{2} N_A \sigma_{\text{HC}} P} \quad 31.3.27$$

As the pressure increases the molecules are closer together, which increases the collision rate and shortens the mean free path. The mean free path has important practical consequences. For example in a time-of-flight mass spectrometer, a molecular ion must travel from the ionization source to the detector without a collision. The time-of-flight analyzer must be kept at a very low pressure to reduce the collision rate of the molecular ion with residual air in the flight tube.

Example 31.3.3: Mean Free Path

Determine the pressure required to increase the mean free path in residual air to 1.00 m in a time-of-flight mass analyzer at 298 K. Assume residual air is essentially pure N_2 with the hard-core collision diameter $d_{\text{N}_2} = (2r_{\text{N}_2}) = 3.75 \text{ \AA}$.

Answer: The collision cross-section, using Eq. 31.3.6:

$$\sigma_{\text{HC}} = \pi (2r_{\text{A}})^2 = \pi [3.75 \times 10^{-10} \text{ m}]^2 = 4.418 \times 10^{-19} \text{ m}^2 = 0.442 \text{ nm}^2 = 44.2 \text{ \AA}^2$$

Using Eq. 31.3.27 the required pressure is:

$$\begin{aligned} P &= \frac{RT}{\sqrt{2} N_A \sigma_{\text{HC}} \lambda} = \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.2 \text{ K})}{\sqrt{2} 6.022 \times 10^{23} \text{ mol}^{-1} (4.418 \times 10^{-19} \text{ m}^2) 1.00 \text{ m}} \\ &= 6.59 \times 10^{-3} \text{ N m}^{-2} = 6.59 \times 10^{-3} \text{ Pa} = 6.59 \times 10^{-8} \text{ bar} \end{aligned}$$

In alternate units: $P = 6.59 \times 10^{-8} \text{ bar} (1 \text{ atm}/1.01325 \text{ bar}) = 6.50 \times 10^{-8} \text{ atm} = 4.94 \times 10^{-5} \text{ torr}$

31.4 The Distribution of Molecular Kinetic Energies Has a Maximum

The Maxwell distribution of molecular speeds can be converted into a distribution function of translational kinetic energies. The distribution function of kinetic energies lends insight into the energy available from collisions that is available to initiate bond rearrangements. The speed and

kinetic energy are related through $\varepsilon_t = \frac{1}{2} mc^2$. To change variables in Eq. 31.2.26 from c to ε_t , the derivative of the energy with respect to speed is:

$$\frac{d\varepsilon_t}{dc} = mc = (2m\varepsilon_t)^{1/2} \quad \text{giving} \quad dc = (2m\varepsilon_t)^{-1/2} d\varepsilon_t \quad \text{while} \quad c^2 = \frac{\varepsilon_t}{m} \quad 31.4.1$$

Substituting the definition of the kinetic energy and using Eqs. 31.4.1 for the differential and c^2 gives the distribution of kinetic energies as:

$$p(\varepsilon_t) d\varepsilon_t = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\varepsilon_t/kT} \frac{\varepsilon_t}{2m} (2m\varepsilon_t)^{-1/2} d\varepsilon_t \quad 31.4.2$$

Collecting terms gives the Maxwell distribution of translational kinetic energy:

$$p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} e^{-\varepsilon_t/kT} \varepsilon_t^{1/2} d\varepsilon_t \quad 31.4.3$$

The distribution function depends only on temperature: at the same temperature all ideal gases have the same kinetic energy. The distribution is the product of a decreasing function, $e^{-\varepsilon_t/kT}$, and an increasing function, $\varepsilon_t^{1/2}$, so that the distribution has a maximum, Figure 31.4.1. Similarly, we also found a maximum in the distribution of molecular velocities. The fraction of molecules with large kinetic energies is small.

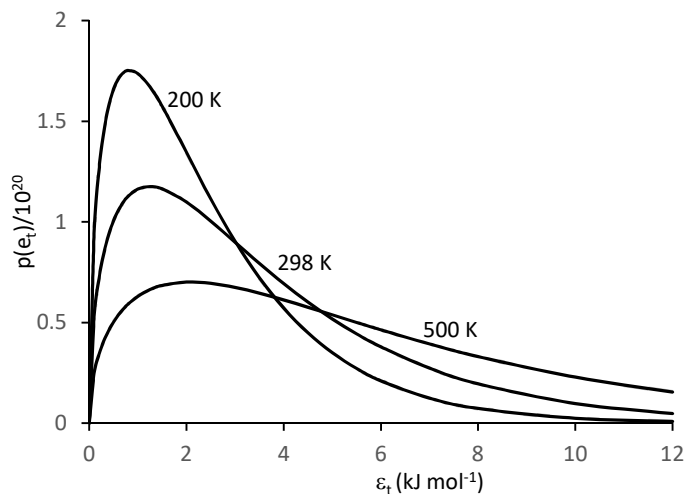


Figure 31.4.1: Maxwell distribution of translational kinetic energy in an ideal gas. The most probable kinetic energy is $\varepsilon_{mp} = kT/2$.

Using the Maxwell distribution of kinetic energies, Eq. 31.4.3, the average translational kinetic energy of an ideal gas is:

$$\overline{\varepsilon_t} = \int_0^{\infty} \varepsilon_t p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \int_0^{\infty} \varepsilon_t^{3/2} e^{-\varepsilon_t/kT} d\varepsilon_t \quad 31.4.4$$

We can simplify the integral with the change in variables $\varepsilon_t = x^2$ or equivalently $x = \varepsilon_t^{1/2}$, giving:

$$\frac{d\varepsilon_t}{dx} = \frac{dx^2}{dx} = 2x \quad \text{giving} \quad d\varepsilon_t = 2x \, dx \quad \text{while} \quad \varepsilon_t^{3/2} = x^3 \quad 31.4.5$$

Substituting the expressions for the change of variables into Eq. 31.4.4 gives:

$$\bar{\varepsilon}_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} 2 \int_0^\infty x^4 e^{-x^2/kT} dx \quad 31.4.6$$

Standard tables give the integral as $\int_0^\infty x^4 e^{-ax^2} dx = \frac{3}{8a^2} \left(\frac{\pi}{a} \right)^{1/2}$, which upon substitution gives:

$$\bar{\varepsilon}_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} 2 \frac{3(kT)^2}{8} (\pi kT)^{1/2} = 3/2 kT \quad 31.4.7$$

which is exactly the result that we expect from experiments on monatomic gases and from Equipartition. The importance of this expression, however, is that the result is derived from first principles. No experimental information, such as the ideal gas law, is used in the derivation. In fact we can now derive the ideal gas law.

The PV product of an ideal gas is given by Eq. 31.1.15. Substitution of Eq. 31.4.7 into Eq. 31.1.15 gives the ideal gas law without any dependence on experimental information:

$$PV = 1/3 N m \bar{u}^2 = 2/3 N \bar{\varepsilon}_t = NkT = nRT \quad 31.4.8$$

This derivation of the ideal gas law also shows that the relationships that we have developed for the average speed and the rms-speed are also from first principles.

Eq. 31.3.21 gives an upper limit for the bimolecular rate constant, because many collisions are unsuccessful at producing products. Consider the possibility that for a successful reaction, sufficient energy must be available from the translational kinetic energy of the collision to bring about the bond breaking and making steps. In the next chapter we will relate this minimum collisional energy to the activation energy of the reaction. A typical activation energy is 50 kJ mol^{-1} , while at room temperature RT is only 2.48 kJ mol^{-1} . The fraction of the molecules in an ideal gas that have translational kinetic energies above a given threshold, ε^* , is given by integrating the Maxwell distribution from ε^* to ∞ . This integral has no closed form solution and must be integrated numerically. However, if the threshold energy is large compared to $3kT$, the integral is adequately approximated as (see the Problems):^{1,2}

$$p(\varepsilon_t > \varepsilon^*) = \int_{\varepsilon^*}^\infty p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \int_{\varepsilon^*}^\infty \varepsilon_t^{1/2} e^{-\varepsilon_t/kT} d\varepsilon_t \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT} \right)^{1/2} e^{-\varepsilon^*/kT} \quad (\varepsilon^* > 3kT) \quad 31.4.9$$

At room temperature, if the threshold energy is 50 kJ mol^{-1} , the fraction of molecules with energies greater than the threshold is only 4×10^{-8} . Relatively few molecules are sufficiently energy rich. However, this fraction is roughly an exponentially increasing function of temperature. At 500 K with the threshold again at 50 kJ mol^{-1} , the fraction of molecules with energy greater than the threshold is 8×10^{-5} , or a factor of 2000 greater than at room temperature. We need to take into account that the appropriate kinetic energy is the relative collision energy, and not the kinetic energy of a single molecule. However, Eq. 31.4.9 is helpful in understanding why reactions are often slow. We should also remember that not all reactions have an activation energy.

31.5 Center of Mass Coordinates²

Only the relative motion of two colliding molecules is significant. The motion of the center of mass of the two molecules makes no contribution to the collision. The purpose of transforming to center of mass coordinates is to allow us to focus on the relative motion of the two molecules. The mass of molecule 1 is m_1 and the mass of molecule 2 is m_2 . The total mass is $M = m_1 + m_2$. The position of molecule 1 is specified by position vector 1, \vec{r}_1 and the position molecule 2 by \vec{r}_2 . The vector velocities of the two molecules are the derivatives of position with respect to time:

$$\vec{v}_1 = \frac{d\vec{r}_1}{dt} \quad \text{and} \quad \vec{v}_2 = \frac{d\vec{r}_2}{dt} \quad 31.5.1$$

The relative velocity of the two molecules is the vector difference $\vec{v}_{\text{rel}} = \vec{v}_1 - \vec{v}_2$, Figure 31.5.1b. The speeds are the magnitudes of the velocity vectors. The speed corresponding to \vec{v}_{rel} is:

$$c_{\text{rel}}^2 = v_{x,\text{rel}}^2 + v_{y,\text{rel}}^2 + v_{z,\text{rel}}^2 = \vec{v}_{\text{rel}} \cdot \vec{v}_{\text{rel}} = \vec{v}_{\text{rel}}^2 \quad 31.5.2$$

where $\vec{v}_{\text{rel}} \cdot \vec{v}_{\text{rel}}$ is the vector dot product, which is commonly symbolized as \vec{v}_{rel}^2 . The velocity of the center of mass, COM, is determined from:

$$M \vec{v}_{\text{com}} = m_1 \vec{v}_1 + m_2 \vec{v}_2 \quad 31.5.3$$

If molecule 1 is heavier, the center of mass lies closer to molecule 1 than molecule 2; in other words, if $m_1 > m_2$ the weighting in the last equation favors the $m_1 \vec{v}_1$ term in the sum. We now need to show that the kinetic energy during the collision is the sum of the kinetic energy of the center of mass and the relative kinetic energy of the colliding molecules:

$$\epsilon_t = \frac{1}{2} M c_{\text{com}}^2 + \frac{1}{2} \mu c_{\text{rel}}^2 \quad 31.5.4$$

where μ is the reduced mass of the collision, Eq. 31.3.13. Only the relative kinetic energy is available to meet the activation energy demand.

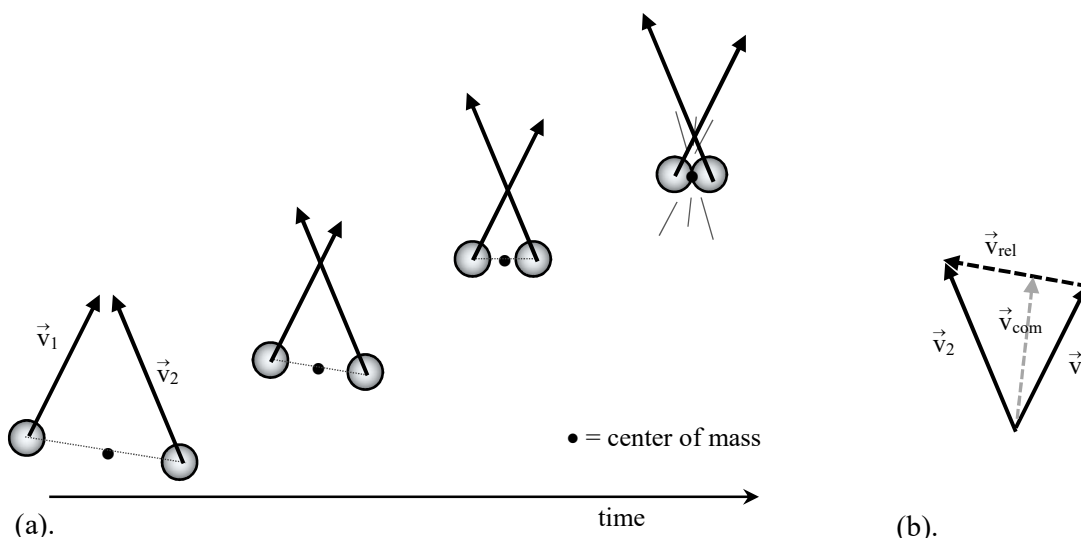


Figure 31.5.1: Center of mass coordinates. (a). Laboratory reference-frame time-course of the collision. The four diagrams are snapshots at successive time intervals. (b). The velocity vectors are translated to a common origin. Then the relative velocity vector is $\vec{v}_{\text{rel}} = \vec{v}_1 - \vec{v}_2$.

The first step is to determine the relative motion of each velocity vector compared to the center of mass. Given that the total mass is $M = m_1 + m_2$, then:

$$\frac{m_1}{M} + \frac{m_2}{M} = 1 \quad 31.5.5$$

The motion of molecule 2 relative to the center of mass is:

$$\vec{v}_2 - \vec{v}_{\text{com}} = \left(\frac{m_1}{M} + \frac{m_2}{M} \right) \vec{v}_2 - \vec{v}_{\text{com}} = \frac{m_1}{M} \vec{v}_2 + \frac{m_2}{M} \vec{v}_2 - \vec{v}_{\text{com}} \quad 31.5.6$$

Dividing Eq. 31.5.3 by M and rearranging gives:

$$\frac{m_2}{M} \vec{v}_2 - \vec{v}_{\text{com}} = -\frac{m_1}{M} \vec{v}_1 \quad 31.5.7$$

Substitution of this last equation into the last two terms in Eq. 31.5.6 gives, Figure 31.5.2:

$$\begin{aligned} \vec{v}_2 - \vec{v}_{\text{com}} &= \frac{m_1}{M} \vec{v}_2 - \frac{m_1}{M} \vec{v}_1 = \frac{m_1}{M} (\vec{v}_2 - \vec{v}_1) \\ &= \frac{m_1}{M} \vec{v}_{\text{rel}} \end{aligned} \quad 31.5.8$$

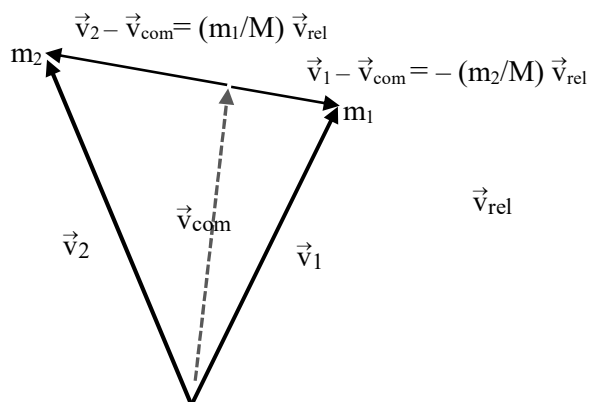


Figure 31.5.2: The relative motion of each velocity vector compared to the center of mass: the vector differences are $\vec{v}_1 - \vec{v}_{\text{com}}$ and $\vec{v}_2 - \vec{v}_{\text{com}}$.

Repeating the steps in Eqs. 31.5.5-31.5.8 for molecule 1 gives:

$$\vec{v}_1 - \vec{v}_{\text{com}} = -\frac{m_2}{M} \vec{v}_{\text{rel}} \quad 35.5.9$$

Solving 35.5.9 for \vec{v}_1 and Eq. 31.5.8 for \vec{v}_2 gives:

$$\vec{v}_1 = \vec{v}_{\text{com}} - \frac{m_2}{M} \vec{v}_{\text{rel}} \quad \text{and} \quad \vec{v}_2 = \vec{v}_{\text{com}} + \frac{m_1}{M} \vec{v}_{\text{rel}} \quad 35.5.10$$

The total kinetic energy is given by:

$$\epsilon_t = \frac{1}{2} m_1 \vec{v}_1^2 + \frac{1}{2} m_2 \vec{v}_2^2 \quad 35.5.11$$

where \vec{v}_1^2 and \vec{v}_2^2 are the corresponding dot products. Substituting Eqs. 35.5.10 for \vec{v}_1 and \vec{v}_2 into the last equation gives:

$$\epsilon_t = \frac{1}{2} m_1 \left(\vec{v}_{\text{com}} - \frac{m_2}{M} \vec{v}_{\text{rel}} \right)^2 + \frac{1}{2} m_2 \left(\vec{v}_{\text{com}} + \frac{m_1}{M} \vec{v}_{\text{rel}} \right)^2 \quad 35.5.12$$

Doing the multiplications and collecting terms gives (a bit of a mess, frankly):

$$\epsilon_t = \frac{1}{2} m_1 \vec{v}_{\text{com}}^2 - \frac{2m_1 m_2}{2M} \vec{v}_{\text{rel}} \cdot \vec{v}_{\text{com}} + \frac{m_1 m_2^2}{2M^2} \vec{v}_{\text{rel}}^2 + \frac{1}{2} m_2 \vec{v}_{\text{com}}^2 + \frac{2m_2 m_1}{2M} \vec{v}_{\text{rel}} \cdot \vec{v}_{\text{com}} + \frac{m_2 m_1^2}{2M^2} \vec{v}_{\text{rel}}^2 \quad 35.5.13$$

Giving $M = m_1 + m_2$, the terms in combine to give the kinetic energy of the center of mass motion. The cross terms in $\vec{v}_{\text{rel}} \cdot \vec{v}_{\text{com}}$ cancel. The remaining terms in \vec{v}_{rel}^2 have a common factor of $m_1 m_2$. Again using $M = m_1 + m_2$, finally gives:

$$\begin{aligned} \epsilon_t &= \frac{1}{2} M \vec{v}_{\text{com}}^2 + \frac{m_1 m_2 M}{2M^2} \vec{v}_{\text{rel}}^2 = \frac{1}{2} M \vec{v}_{\text{com}}^2 + \frac{m_1 m_2}{2M} \vec{v}_{\text{rel}}^2 \\ \epsilon_t &= \frac{1}{2} M \vec{v}_{\text{com}}^2 + \frac{1}{2} \mu \vec{v}_{\text{rel}}^2 \end{aligned} \quad 35.5.14$$

Substituting the square scalar speeds for the dot products gives Eq. 31.5.4.

To gain some appreciation for the center of mass frame of reference, picture an otherwise darkened room with only two bumper cars in view. Assume that the velocity vectors of the cars are as shown in Figure 31.5.1, the cars are rolling forward while tending towards each other. You sit on a sled that travels with the center of mass. Because the room is dark, you don't notice that you are moving forwards. One bumper car is on your left and one on your right. What would you observe as time advances? The bumper cars appear to move directly towards you with a speed given by the relative speed. You are all traveling forwards, but only the relative motion matters and then you find yourself in the middle of the collision.

The center of mass frame is convenient when dealing with collisions. However, is the probability distribution of the relative speed still given by the corresponding Maxwell distribution? Using the identity $e^{a+b} = e^a e^b$ with Eq. 31.5.4, the Maxwell weighting factor gives the probability distribution as a function of:

$$e^{-\epsilon_t/kT} = e^{-(Mc_{\text{com}}^2 + \mu c_{\text{rel}}^2)/2kT} = e^{-Mc_{\text{com}}^2/2kT} e^{-\mu c_{\text{rel}}^2/2kT} \quad 31.5.15$$

Upon normalization the Maxwell distribution is given by:

$$\begin{aligned} p(\mathbf{v}_{\text{com},x}, \mathbf{v}_{\text{com},y}, \mathbf{v}_{\text{com},z}, \mathbf{v}_{\text{rel},x}, \mathbf{v}_{\text{rel},y}, \mathbf{v}_{\text{rel},z}) & d\mathbf{v}_{\text{com},x} d\mathbf{v}_{\text{com},y} d\mathbf{v}_{\text{com},z} d\mathbf{v}_{\text{rel},x} d\mathbf{v}_{\text{rel},y} d\mathbf{v}_{\text{rel},z} \\ &= \left(\frac{M}{2\pi kT} \right)^{3/2} \left(\frac{\mu}{2\pi kT} \right)^{3/2} e^{-Mc_{\text{com}}^2/2kT} e^{-\mu c_{\text{rel}}^2/2kT} d\mathbf{v}_{\text{com},x} d\mathbf{v}_{\text{com},y} d\mathbf{v}_{\text{com},z} d\mathbf{v}_{\text{rel},x} d\mathbf{v}_{\text{rel},y} d\mathbf{v}_{\text{rel},z} \end{aligned} \quad 31.5.16$$

which parallels Eq. 31.2.12 for this two-particle distribution. The distribution function is separable in the center of mass and relative coordinates. Fortunately, we don't need to know about the velocity of the center or mass; only the relative motion has an effect on the collision. Integrating over the center of mass velocity components gives the distribution function of the

relative speed. The center of mass portion of the Maxwell distribution integrates to unity, since the distribution is normalized:

$$\begin{aligned} & p(\mathbf{v}_{\text{rel},x}, \mathbf{v}_{\text{rel},y}, \mathbf{v}_{\text{rel},z}) \, d\mathbf{v}_{\text{rel},x} \, d\mathbf{v}_{\text{rel},y} \, d\mathbf{v}_{\text{rel},z} \\ &= \left(\frac{M}{2\pi kT}\right)^{3/2} \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\mu c_{\text{rel}}^2/2kT} \, d\mathbf{v}_{\text{rel},x} \, d\mathbf{v}_{\text{rel},y} \, d\mathbf{v}_{\text{rel},z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-Mc_{\text{com}}^2/2kT} \, d\mathbf{v}_{\text{com},x} \, d\mathbf{v}_{\text{com},y} \, d\mathbf{v}_{\text{com},z} \\ &= \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\mu c_{\text{rel}}^2/2kT} \, d\mathbf{v}_{\text{rel},x} \, d\mathbf{v}_{\text{rel},y} \, d\mathbf{v}_{\text{rel},z} \end{aligned} \quad 31.5.17$$

Conversion to spherical polar coordinates is often convenient:

$$p(c_{\text{rel}}) \, dc_{\text{rel},x} \, d\theta \, d\phi = \left(\frac{\mu}{2\pi kT}\right)^{3/2} e^{-\mu c_{\text{rel}}^2/2kT} \, c_{\text{rel}}^2 \sin\theta \, dc_{\text{rel}} \, d\theta \, d\phi \quad 31.5.18$$

For an isotropic system, the angular integrals then reduce to 4π using Eq. 31.2.23:

$$p(c_{\text{rel}}) \, dc_{\text{rel}} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\mu c_{\text{rel}}^2/2kT} \, c_{\text{rel}}^2 \, dc_{\text{rel}} \quad 31.5.19$$

The result is identical to the Maxwell distribution of molecular speeds of a single particle, Eq. 31.2.16, except that the relevant random variable is now the relative speed and the mass of the particle is replaced by the reduced mass, μ .

31.6 Derivation of the Maxwell Distribution from the Particle In a Box³

The Maxwell distribution of translational kinetic energies, Eq. 31.4.3, is one of the central equations in physical chemistry. We developed this important equation using a change of variables from the distribution of molecular velocities, the form for which was suggested by analogy with the quantum Boltzmann distribution of the particle in a box. A rigorous derivation of the Maxwell distribution from the Boltzmann distribution is instructive for two reasons. First, the interrelationship of the quantum and macroscopic worlds is delineated and second, the derivation requires the density of states. We introduced the density of states concept in Secs. 28.3 and 28.6. Particle in a box energy states are highly degenerate and essentially continuous near room temperature, giving a large density of states, Figure 31.6.1.

The quantum mechanical energy of a particle in a cubical box with side length a is a function of the three quantum numbers, n_x , n_y , and n_z :

$$\varepsilon_t = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8ma^2} n^2 \quad (23.6.17) \quad 31.6.1$$

For convenience, the quantum numbers are combined into a single variable using the definition $n^2 \equiv (n_x^2 + n_y^2 + n_z^2)$.

The Boltzmann distribution of a 3D-particle in a box is the product of the one-dimensional expressions, Eq. 31.2.7, for each direction:

$$p_i = \frac{n_i}{N} = \frac{e^{-\varepsilon_i/kT}}{(2\pi mkT)^{3/2} V/h^3} \quad \varepsilon_t = \varepsilon_x + \varepsilon_y + \varepsilon_z = \frac{1}{2} m(\mathbf{v}_x^2 + \mathbf{v}_y^2 + \mathbf{v}_z^2) \quad 31.6.2$$

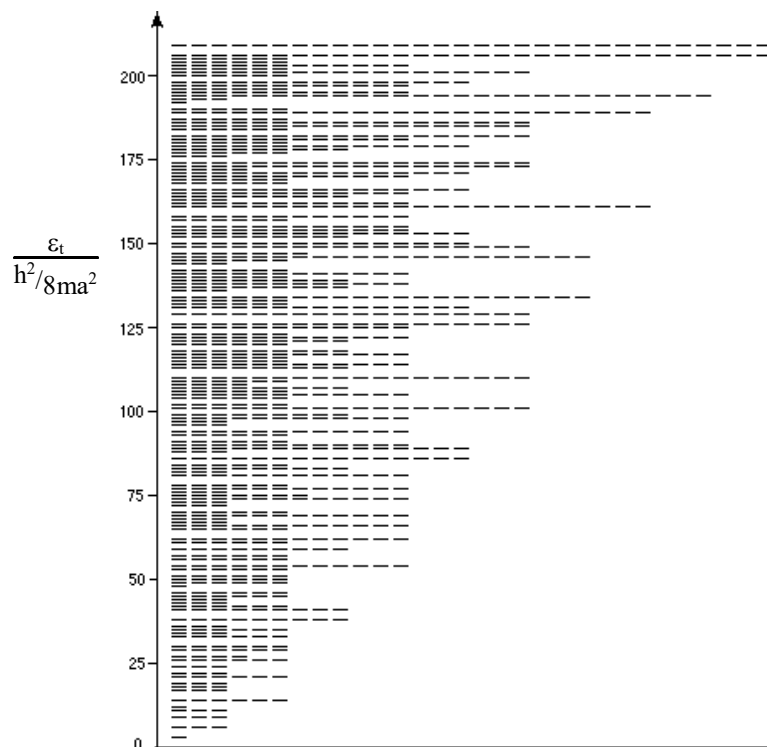


Figure 31.6.1: Particle in a cubical box energy states are highly degenerate and essentially continuous near room temperature, giving a large density of states increasing with ϵ_i .⁴

The translational energy levels of macroscopic systems are essentially continuous, so that averages over the distribution function can be determined using integrals rather than summations. In converting the quantum distribution to a continuous distribution, the differential of the continuous variable, dn , is introduced:

$$p(\epsilon_i) dn = \frac{n_i}{N} dn = \frac{e^{-\epsilon_i/kT}}{(2\pi mkT)^{3/2} V/h^3} dn \quad 31.6.3$$

To complete the change in variables from the quantum numbers to a kinetic energy distribution, the density of states, $\rho(\epsilon_i)$, is required:

$$dn = \frac{dn}{d\epsilon_i} d\epsilon_i = \rho(\epsilon_i) d\epsilon_i \quad (28.3.3) \quad 31.6.4$$

The density of states is the number of quantum states in the energy range from ϵ_i to $\epsilon_i + d\epsilon_i$. From a different perspective, the density of states is just the derivative that is required to do a normal change of variables in an integral. The derivative is difficult to do directly. Instead, let $N(\epsilon_i)$ be the number of states from zero energy up to energy ϵ_i . Both dn and $dN(\epsilon_i)$ give the change in number of quantum states at energy ϵ_i . The density of states is then the derivative:

$$\rho(\epsilon_i) = \frac{dN(\epsilon_i)}{d\epsilon_i} \quad (28.3.3) \quad 31.6.5$$

The number of quantum states up to energy ϵ_t can be determined using a graphical analogy, Figure 31.6.2. Each choice of quantum numbers, n_x , n_y , n_z is represented as a point in an x-y-z coordinate plot, Figure 31.6.2a. Each unit change of n_x , n_y , and n_z corresponds to a unit volume cube. Each unit of volume corresponds to one specific value of n_x , n_y , and n_z . The maximum value of n for states with energy less than or equal to ϵ_t is calculated by solving Eq. 31.6.1 for n :

$$n_{\max} = (8m)^{1/2} \left(\frac{a}{h} \right) \epsilon_t^{1/2} \quad 31.6.6$$

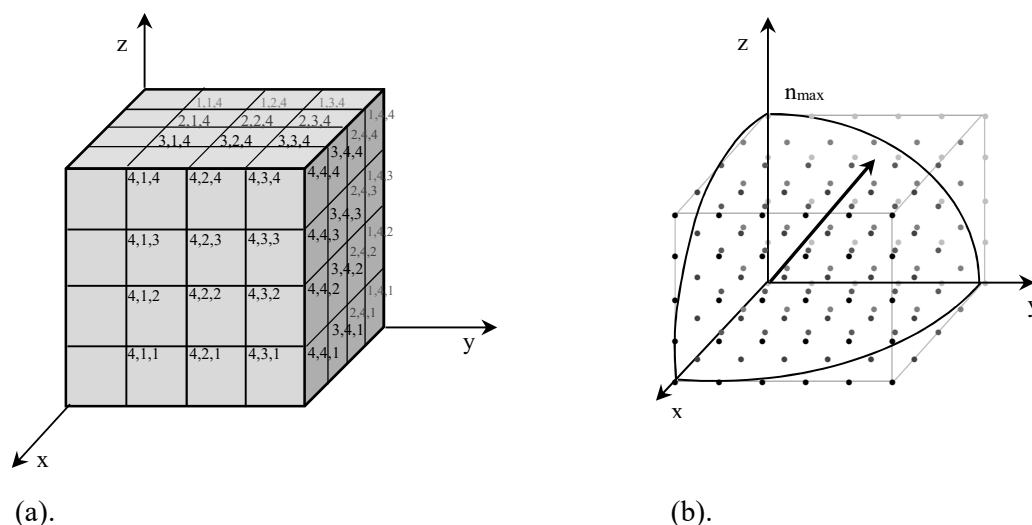


Figure 31.6.2: (a). Each possible set of quantum numbers lies at the corner of a cube of unit volume. Each translational state corresponds to a set of quantum numbers, n_x , n_y , n_z . The total volume equals the number of states. (b). Only positive quantum numbers are possible. The total number of states with energy from 0 to ϵ_t is $1/8$ volume of a sphere of radius n_{\max} .

The total number of states with energies between zero and ϵ_t is given by $1/8$ of the volume of the sphere with radius n_{\max} , Figure 31.6.2b. The factor of $1/8$ is necessary because a sphere centered on the origin is divided into octants, but only one-octant has all positive x , y , z values. The volume of a sphere is $4/3\pi r^3$, which gives the number of states with energy from zero to ϵ_t as:

$$N(\epsilon_t) = \frac{1}{8} \left(\frac{4}{3} \pi n_{\max}^3 \right) = \left(\frac{\pi}{6} \right) (8m)^{3/2} \left(\frac{a}{h} \right)^3 \epsilon_t^{3/2} = \left(\frac{\pi}{6} \right) (8m)^{3/2} \frac{V}{h^3} \epsilon_t^{3/2} \quad 31.6.7$$

The density of states is the derivative with respect to ϵ_t , Eq. 31.6.5:

$$\rho(\epsilon_t) = \frac{dN(\epsilon_t)}{d\epsilon_t} = \left(\frac{\pi}{6} \right) (8m)^{3/2} \frac{V}{h^3} \left(\frac{3}{2} \right) \epsilon_t^{1/2} = \frac{\pi}{4} (8m)^{3/2} \frac{V}{h^3} \epsilon_t^{1/2} \quad 31.6.8$$

The density of states increases with increasing kinetic energy; this increase is also observable in Figure 31.6.1. The density of translational states is quite large for macroscopic systems; molecules are in an extensive “bath” of available translational states. Substituting the density of states into Eq. 31.6.3 gives the probability of occurrence of a molecule with translational energy ϵ_t as:

$$p(\varepsilon_t) d\varepsilon_t = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT)^{3/2} V/h^3} \rho(\varepsilon_t) d\varepsilon_t = \frac{e^{-\varepsilon_t/kT}}{(2\pi mkT)^{3/2} V/h^3} \frac{\pi}{4} (8m)^{3/2} \frac{V}{h^3} \varepsilon_t^{1/2} d\varepsilon_t \quad 31.6.9$$

Canceling common terms gives the Maxwell distribution of translational kinetic energy:

$$p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} e^{-\varepsilon_t/kT} \varepsilon_t^{1/2} d\varepsilon_t \quad (31.4.3)$$

The $e^{-\varepsilon_t/kT}$ factor decreases strongly with increasing energy; high energy states are less probable than low energy states. However, the density of translational states increases as $\varepsilon_t^{1/2}$, giving a maximum in the distribution function at thermodynamically significant energies, Figure 31.4.1. This derivation shows that the quantum and macroscopic views are completely consistent. While we live in a quantum world, under practical circumstances translational quantum states become essentially continuous and classical mechanics often provides an accurate description.

31.7 Summary – Looking Ahead

The kinetic molecular theory description of the pressure of an ideal gas seems an unassuming beginning of the foundations of physical chemistry. However, KMT is the first historical instance of a rigorous molecular description of matter. The microscopic structure of atoms and molecules is reflected in all chemical processes. KMT is based on the Maxwell distribution functions of molecular velocity and of translational kinetic energy. Distribution functions are inherently statistical descriptions of the underlying degrees of freedom. Molecules are in a “bath” of available translational states. Molecules occupy the available states at random. The statistical distribution of available thermal kinetic energy, as defined by the temperature, is the key to understanding the underlying form of chemistry. In this way, KMT provides the foundations of modern statistical mechanics. For example, the Maxwell distribution is the cornerstone of modern theories of protein motion.

This pattern is common in the physical sciences. Old theories and models are often found to be a subset of new theories. New theories don’t necessarily invalidate old theories. The old theories are valid within a specific “realm of applicability” or “realm of convenience.” For macroscopic scale chemical phenomena, molecular translation lies within the realm of convenience of classical theory, except at temperatures near absolute zero.

We have completely overlooked an important aspect of kinetic molecular theory. KMT plays a central role in understanding gas phase transport phenomena, including viscosity, thermal conductivity, and diffusion. Historically viscosity provided an important window into intermolecular forces and the role of fluctuations in kinetic phenomena. However, these applications are outside our primary focus on chemical reactivity. We must leave these important areas to your further study.

Kinetic molecular theory provides an upper limit to the value of the bimolecular rate constants of ideal gas reactions. KMT is an excellent start towards predicting how often collisions occur. However, many factors contribute to the successful production of products in a chemical reaction. The rotational and vibrational energies of the reactants, the timing of the collision with respect to the rotational and vibrational motions, and the collision energy all play critical roles. Many collisions, if not most collisions, are unsuccessful at producing products. The concept of a transition state is a key insight for discussing the progress of the bond breaking and making steps

after the onset of the collision. Chemical reaction dynamics and the properties of the transition state are the subject of the next chapter.

Chapter Summary

1. The kinetic molecular theory assumptions are: Molecules in a gas are point masses with no volume in constant, random, rapid, isotropic motion. No forces act between molecules, except at the instant of a collision. Collisions are instantaneous and elastic.
2. The assumption of negligible molecular volume is relaxed for intermolecular collisions.
3. The pressure in Pa of an ideal gas of mass m and molar mass \mathcal{M} , with N molecules in a container of volume V having rms-speed u is:

$$P = \frac{Nm\overline{c^2}}{3V} = \frac{Nmu^2}{3V} = \frac{n\mathcal{M}u^2}{3V} \quad u = (\overline{c^2})^{1/2}$$

4. The average translational kinetic energy of a molecule is $\overline{\varepsilon}_t = \frac{1}{2} m\overline{c^2} = \frac{1}{2} mu^2$.
5. The ideal gas law is: $PV = \frac{1}{3} N mu^2 = \frac{2}{3} N \overline{\varepsilon}_t = nRT$ giving $\overline{\varepsilon}_t = \frac{3}{2} kT$.
6. The one-dimensional Maxwell distribution function of molecular velocities is:

$$p(v_x) dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x$$

7. Spherical polar coordinates span the ranges: $0 \leq c \leq \infty$, $0 \leq \theta \leq \pi$, $0 \leq \phi \leq 2\pi$.
8. The transformation between spherical polar coordinates and Cartesian coordinates is:

$$c = \sqrt{v_x^2 + v_y^2 + v_z^2} \quad v_x = c \sin \theta \cos \phi \quad v_y = c \sin \theta \sin \phi \quad v_z = c \cos \theta$$
9. The volume element in “three-space” in spherical polar coordinates: $d\tau = c^2 \sin \theta dc d\theta d\phi$.
10. The angular integral over all space is: $\int_0^\pi \int_0^{2\pi} \sin \theta d\theta d\phi = 4\pi$, giving 4π radians in a sphere.
11. The Maxwell distribution of molecular speeds is: $p(c) dc = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT} c^2 dc$
12. The most probable, average, and rms-speeds, with m in kg or \mathcal{M} in kg mol⁻¹, are:

$$c_{mp} = \sqrt{\frac{2kT}{m}} \quad \overline{c} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi \mathcal{M}}} \quad u = (\overline{c^2})^{1/2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{\mathcal{M}}}$$

13. The rate of collisions with a wall for a molecule with velocity v_x per unit area is $= \frac{N}{V} v_x$.

14. The ideal gas law gives the number density as: $N/V = N_A P/RT$.

15. The average collision rate with a wall per unit area is: $Z_{wall} = \frac{N}{V} \left(\frac{kT}{2\pi m}\right)^{1/2} = \frac{1}{4} \frac{N}{V} \overline{c}$

16. For a hole with cross-sectional area A , the rate of effusion in mol s⁻¹ is:

$$\frac{dn}{dt} = \frac{Z_{wall} A}{N_A} = P A \left(\frac{1}{2\pi \mathcal{M} RT}\right)^{1/2}$$

For a gas mixture, the pressure P is replaced by the partial pressure of the substance, P_i .

17. The relative effusion rate of n_1 moles of molecule 1 at pressure P_1 and n_2 moles of molecule 2 at pressure P_2 is:

$$\frac{\text{effusion rate 2}}{\text{effusion rate 1}} = \frac{n_2}{n_1} \left(\frac{\mathcal{M}_1}{\mathcal{M}_2} \right)^{1/2} = \frac{P_2}{P_1} \left(\frac{\mathcal{M}_1}{\mathcal{M}_2} \right)^{1/2}$$

18. A collision occurs if molecules with radii r_A and r_B approach within the hard-core collision cross section, $\sigma_{\text{HC}} = \pi (r_A + r_B)^2 = \pi d^2$, with d the hard-core collision diameter.

19. The average relative speed with the reduced mass of the colliding pair of molecules, μ , is:

$$\bar{c}_{\text{rel}} = \left(\frac{8kT}{\pi\mu} \right)^{1/2} \quad \mu = \frac{m_A m_B}{m_A + m_B} = \left(\frac{\mathcal{M}_A \mathcal{M}_B}{\mathcal{M}_A + \mathcal{M}_B} \right) \frac{1}{N_A} \quad (1 \text{ kg}/1000 \text{ g})$$

20. For N_A and N_B molecules of A and B, the A-B collision rate per unit volume is:

$$Z_{AB} = \sigma_{\text{HC}} \bar{c}_{\text{rel}} (N_A/V)(N_B/V) \quad \text{with} \quad N_i/V = N_A P_i/RT$$

21. For A-A collisions the collision rate per unit volume is: $Z_{AA} = \frac{1}{2} \sigma_{\text{HC}} \sqrt{2} \bar{c} (N/V)^2$.

22. Assuming each collision gives products, the hard-core bimolecular reaction rate is:

$$-\frac{d[A]}{dt} = \frac{Z_{AB}}{N_A} = \sigma_{\text{HC}} \bar{c}_{\text{rel}} N_A [A] [B]$$

23. The hard-core bimolecular rate constant in $\text{L mol}^{-1} \text{ s}$ is:

$$k_2 = \sigma_{\text{HC}} \bar{c}_{\text{rel}} N_A = \pi d^2 \left(\frac{8kT}{\pi\mu} \right)^{1/2} (1000 \text{ L}/\text{m}^3) N_A$$

24. The mean free path is: $\lambda = \frac{\bar{c}}{Z_{AA} V/N} = \frac{V}{\sqrt{2} \sigma_{\text{HC}} N} = \frac{RT}{\sqrt{2} N_A \sigma_{\text{HC}} P}$

25. The Maxwell distribution of translational kinetic energy: $p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} e^{-\varepsilon_t/kT} \varepsilon_t^{1/2} d\varepsilon_t$

26. The fraction of molecules with translational kinetic energy exceeding ε^* , if $\varepsilon^* > 3kT$ is:

$$p(\varepsilon_t > \varepsilon^*) = \int_{\varepsilon^*}^{\infty} p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \int_{\varepsilon^*}^{\infty} \varepsilon_t^{1/2} e^{-\varepsilon_t/kT} d\varepsilon_t \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT} \right)^{1/2} e^{-\varepsilon^*/kT}$$

27. For collision partners with velocities \vec{v}_1 and \vec{v}_2 , the relative velocity is $\vec{v}_{\text{rel}} = \vec{v}_1 - \vec{v}_2$ and relative speed is the magnitude of \vec{v}_{rel} using: $c_{\text{rel}}^2 = v_{x,\text{rel}}^2 + v_{y,\text{rel}}^2 + v_{z,\text{rel}}^2 = \vec{v}_{\text{rel}} \cdot \vec{v}_{\text{rel}} = \vec{v}_{\text{rel}}^2$

28. For collision partners with masses m_1 and m_2 , the velocity of the center of mass is determined using $M \vec{v}_{\text{com}} = m_1 \vec{v}_1 + m_2 \vec{v}_2$, with the total mass $M = m_1 + m_2$.

29. The total kinetic energy during the collision is the sum of the kinetic energy of the center of mass and the relative kinetic energy of the colliding molecules: $\varepsilon_t = \frac{1}{2} M c_{\text{com}}^2 + \frac{1}{2} \mu c_{\text{rel}}^2$

30. The distribution function of relative speeds is a Maxwell distribution with the mass of the particle replaced by the reduced mass of the collision partners, μ .

31. The density of states is the number of quantum states in the energy range from ε to $\varepsilon + d\varepsilon$:

$$\rho(\varepsilon) d\varepsilon = \frac{dn}{d\varepsilon} d\varepsilon = \frac{dN(\varepsilon)}{d\varepsilon} d\varepsilon$$

where $N(\varepsilon)$ is the number of states from zero energy up to energy ε .

32. The density of states of translational energy levels is: $\rho(\varepsilon_t) = \frac{\pi}{4} (8m)^{3/2} \frac{V}{h^3} \varepsilon_t^{1/2}$

33. The density of translational states is quite large for macroscopic systems; molecules are in an extensive “bath” of available translational states.

34. The Maxwell distribution of translational kinetic energy is proportional to the density of states of translational energy levels at energy ε_t in the interval $d\varepsilon$:

$$p(\epsilon_t) d\epsilon = \frac{e^{-\epsilon_t/kT}}{(2\pi mkT)^{3/2} V/h^3} \rho(\epsilon_t) d\epsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} e^{-\epsilon_t/kT} \epsilon_t^{1/2} d\epsilon_t$$

35. Distribution functions are statistical descriptions of the underlying degrees of freedom. Molecules are in a “bath” of available translational states. Molecules occupy the available states at random, subject to the available thermal kinetic energy at the given temperature.

Literature Cited:

1. W. Kauzmann, *Thermal Properties of Matter Vol. I: Kinetic Theory of Gases*, Benjamin, New York, NY, 1966. pp. 158-160.
2. P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw Hill, New York, NY, 2001; reprinted by Dover, Mineola, NY, 2006. Chap. 1.
3. T. L. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960, Sec. 4.1.
4. J. H. Noggle, *Physical Chemistry, 3rd Ed.*, Harper Collins, New York, NY, 1996, Figure 11.9
5. W. Kauzmann, *Thermal Properties of Matter Vol. I: Kinetic Theory of Gases*, Benjamin, New York, NY, 1966. App. 5-1, pp. 239-241.

Further Reading:

- W. Kauzmann, *Thermal Properties of Matter Vol. I: Kinetic Theory of Gases*, Benjamin, New York, NY, 1966.
- P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw Hill, New York, NY, 2001; reprinted by Dover, Mineola, NY, 2006.
- R. D. Present, *An Introduction to the Kinetic Theory of Gases*, McGraw-Hill, New York, NY, 1958.

Chapter 31 Kinetic Molecular Theory Problems

1. Calculate the average translational kinetic energy in J, cm⁻¹, and kJ mol⁻¹ and the rms-speed of CO₂ at 298.2 K, assuming ideal gas behavior.
2. Calculate the rate of molecular collisions in a balloon filled with N₂ at 298.2 K given the balloon has a 1.00 L volume at 1.00 bar. The hard-core collision diameter is $d_{N_2} = (2r_{N_2}) = 3.75 \text{ \AA}$.
3. Derive a relationship for the rate of a unimolecular surface-catalyzed reaction of an ideal gas. Assume every collision with the surface gives products and that the rate law is expressed in terms of the gas phase concentration of the reactant in mol L⁻¹.
4. Find the most probable molecular speed using the Maxwell distribution of molecular speeds.
5. (a). Find the standard deviation of the molecular speed of an ideal gas at temperature T in terms of the molar mass. (b). Find the most probable, average, and rms-speeds and standard deviation of the speed of CO₂ at 298.2 K.

6. (a). Show that the rms-speed is given by the pressure P and mass density d by : $u = \sqrt{3P/d}$.
 (b). At 1.01325 bar and 373.2 K the density of water vapor is 598 g m^{-3} . Calculate the rms-speed of water molecules in water vapor.

7. A compound with molar mass of 255.2 g mol^{-1} is placed in a small container that has a hole of radius 0.0500 mm . In 30.0 min at 50.0°C , 0.872 g of the substance effuses from the container. Calculate the vapor pressure of the substance.

8. A compound with a vapor pressure of 1.680 kPa is placed in a small container closed by a metal membrane with a 0.0500 mm radius hole. The initial mass is 123.5 mg . After 30.0 min at 35.0°C the mass decreases to 39.9 mg . Calculate the molar mass of the substance.

9. Integrals of the form $\int_0^{x_c} e^{-ax^2} dx$ are common in determining the probability of occurrence of speeds or energies within a given range. The integral has no closed form solution and must be integrated numerically. The numerical integrals in dimensionless form are tabulated as the error function, $\text{erf}()$, where the error function is defined by:

$$\frac{2}{\sqrt{\pi}} \int_0^t e^{-y^2} dy = \text{erf}(t)$$

The error function is used extensively in statistics and probability. The inside back cover lists a short table. Extensive tables are available in standard reference sources and Excel has an $\text{erf}()$ function. In this regard $\text{erf}()$ is similar to the more familiar functions $\sin()$, $\cos()$, $\exp()$ and $\ln()$, which are all evaluated as power series expansions.

(a). Show that: $\int_0^{x_c} e^{-ax^2} dx = \frac{1}{2} \left(\frac{\pi}{a}\right)^{1/2} \text{erf}(\sqrt{a} x_c)$

(b). Verify the result in part (a) by showing that $\int_0^\infty e^{-ax^2} dx$ gives the result listed in standard integral tables.

(c). Show the probability of a molecule having a velocity in the x -direction in the range $\pm v^*$ is:

$$\int_{-v^*}^{v^*} p(v_x) dv_x = 2 \int_0^{v^*} \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x = \text{erf}\left(\sqrt{mv^{*2}/2kT}\right)$$

(d). Show that the probability of a molecule having a kinetic energy in the x -direction less than or equal to kT is 84.3% . [Hint: note that $\text{erf}(1) = 0.8427$]

10. Derive the integration by parts formula using the following steps: (a). Let u and v be two functions. Using the product rule for the differential $d(uv)$, show that $\int d(uv) = \int v du + \int u dv$.

(b). Finally show that for the integral limits u_1v_1 to u_2v_2 :

$$\int u dv = uv \Big|_{u_1v_1}^{u_2v_2} - \int v du$$

11. Integrals over the Maxwell distribution of molecular speeds are in the general form

$\int_0^t y^2 e^{-y^2} dy$. Use integration by parts, $\int u dv = uv \Big|_{u_1v_1}^{u_2v_2} - \int v du$, with $u = y$ and $dv = (y e^{-y^2} dy)$ to show that: [See the next problem for an application of this relationship.]

$$\frac{4}{\sqrt{\pi}} \int_0^t y^2 e^{-y^2} dy = \operatorname{erf}(t) - \frac{2}{\sqrt{\pi}} t e^{-t^2}$$

12. The probability of occurrence of molecular speeds over a range of values is determined by an integral over the distribution function. (a). Show that the integral of the Maxwell distribution of molecular speeds over the range from $c = 0$ to c^* is:

$$\int_0^{c^*} p(c) dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{c^*} e^{-mc^2/2kT} c^2 dc = \operatorname{erf}(\sqrt{mc^{*2}/2kT}) - \frac{1}{\sqrt{\pi}} \sqrt{\frac{mc^{*2}}{2kT}} e^{-mc^{*2}/2kT}$$

(b). The kinetic energy at the upper limit is $\varepsilon_t^* = \frac{1}{2}mc^{*2}$. Show that the total probability is:

$$\int_0^{c^*} p(c) dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{c^*} e^{-mc^2/2kT} c^2 dc = \operatorname{erf}(\sqrt{\varepsilon_t^*/kT}) - \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon_t^*}{kT} \right)^{1/2} e^{-\varepsilon_t^*/kT}$$

[Hint: use the relationship in the previous problem with the change in variables $y^2 = mc^2/2kT$]

13. Determine the probability that a molecule has a speed equal to or less than the most probable speed. [Hint: Use the relationship in the previous problem, note that $\operatorname{erf}(1) = 0.8427$]

14. The fraction of molecules with translational kinetic energy exceeding ε^* is:^{1,2}

$$p(\varepsilon_t > \varepsilon^*) = \int_{\varepsilon^*}^{\infty} p(\varepsilon_t) d\varepsilon_t = 2\pi \left(\frac{1}{\pi kT} \right)^{3/2} \int_{\varepsilon^*}^{\infty} \varepsilon_t^{1/2} e^{-\varepsilon_t/kT} d\varepsilon_t$$

(a). Use the change of variable $x^2 = \varepsilon_t/kT$ to show: [Hint: see Eq. 31.4.5 for a similar change in variables.]

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2 e^{-x^2} dx$$

(b). Use integration by parts to show: [Hint: let $u = x$ and $dv = x e^{-x^2} dx$]

$$\int_{x^*}^{\infty} x^2 e^{-x^2} dx = -\frac{1}{2} x e^{-x^2} \Big|_{x^*}^{\infty} - (-\frac{1}{2}) \int_{x^*}^{\infty} e^{-x^2} dx$$

(c). Show that: $\int_{x^*}^{\infty} e^{-x^2} dx = \int_0^{\infty} e^{-x^2} dx - \int_0^{x^*} e^{-x^2} dx$

(d). Use integral tables and the definition of the error function: $\frac{2}{\sqrt{\pi}} \int_0^t e^{-x^2} dx = \operatorname{erf}(t)$ to show that:

$$\int_{x^*}^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2} - \frac{\sqrt{\pi}}{2} \operatorname{erf}(x^*)$$

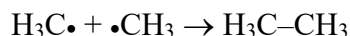
(e). Using the previous expressions, derive the final result:

$$p(\varepsilon_t > \varepsilon^*) = \frac{4}{\sqrt{\pi}} \int_{x^*}^{\infty} x^2 e^{-x^2} dx = \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT} \right)^{1/2} e^{-\varepsilon^*/kT} + 1 - \operatorname{erf} \left(\left[\frac{\varepsilon^*}{kT} \right]^{1/2} \right)$$

(f). Show that for large threshold energies, $\varepsilon^* \gg kT$: $p(\varepsilon_t > \varepsilon^*) \cong \frac{2}{\sqrt{\pi}} \left(\frac{\varepsilon^*}{kT} \right)^{1/2} e^{-\varepsilon^*/kT}$

15. Find the most probable translational kinetic energy of an ideal gas using the Maxwell distribution of translational kinetic energy.

16. The rate constant for the recombination of methyl radicals is $4.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ at 398.2 K.



The reaction has no activation energy. Assuming the hard-core collision radii of the methyl radicals are one-half the normal C–C bond length, $r_{\text{CH}_3} = 0.77 \text{ \AA}$, calculate the bimolecular rate constant assuming hard-core collision theory at 398.2 K.³

17. (a). Show that the density of states of a one-dimensional particle in a box is:

$$\rho(\epsilon_x) d\epsilon_x = (8m)^{1/2} \frac{a}{h} (\epsilon_x)^{-1/2} d\epsilon_x$$

[Hint: you don't need to use the graphical approach that we used for three-dimensions.]

(b). Compare the behavior of the one-dimensional and three-dimensional particle in a box as a function of energy. Why the difference with the change in dimensionality?

18. Calculate the number of translational energy states at 298.2 K for O_2 in a box of volume 1.00 m^3 with energies from kT to $1.001 kT$ (i.e. a 0.1% change in energy).

19. (a). For a square box with side length a and area $A = a^2$, show that the density of states of a two-dimensional particle in a box is:

$$\rho(\epsilon_t) d\epsilon_t = 2\pi m \frac{A}{h^2} d\epsilon_t$$

The two-dimensional case has some applicability to free translational motion on a surface and electrical conduction in restricted geometries. (b). The density of states of a one-dimensional particle in a box is given in the previous problem. Compare the one, two, and three-dimensional cases in terms of the behavior with respect to increasing energy. (c). Find the two-dimensional Maxwell distribution of translational kinetic energy.

Literature Cited:

1. W. Kauzmann, *Thermal Properties of Matter Vol. I: Kinetic Theory of Gases*, Benjamin, New York, NY, 1966. Sec. 4.4
2. P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, McGraw Hill, New York, NY, 2001; reprinted by Dover, Mineola, NY, 2006. Chap. 1.
3. G. M. Barrow, *Physical Chemistry, 6th Ed.*, McGraw-Hill, New York, NY, 1996, p. 822 Problem 16-7.

[Page left intentionally blank]