Lecture 32: More Gas Kinetics

Collision Frequency, Mean Free Path, Total Collision Frequency

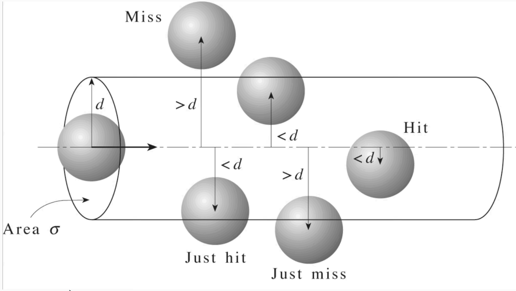
Collision Frequnecy

Assume other particles are stationary. Number of collisions for a single particle in time dt:

$$dN_{\text{coll}} = \rho \cdot dV = \rho \cdot \sigma \langle u \rangle \, dt$$

Using the Maxwell-Boltzmann average speed

$$\langle u \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$



$$dL = \langle u \rangle dt$$

Collision frequency (collisions per particle per unit time):

$$Z_A = \frac{dN_{\text{coll}}}{dt} = \rho\sigma\langle u \rangle = \rho\sigma\sqrt{\frac{8k_B T}{\pi m}}$$

Collision Frequnecy

All particles move, replace m for reduced mass μ:

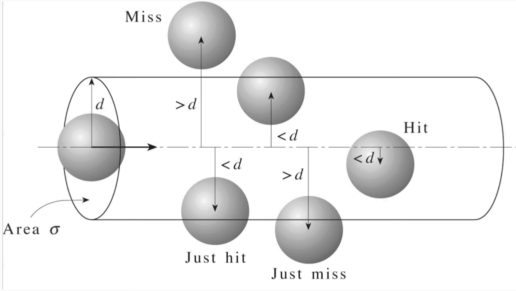
$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2}$$

Relative average speed:

$$\langle u_r \rangle = \sqrt{\frac{8k_BT}{\pi\mu}} = \sqrt{\frac{8k_BT}{\pi\frac{m}{2}}} = \sqrt{2}\,\langle u \rangle$$

Substituting into collision frequency:

$$Z_A = \rho\sigma\langle u_r \rangle = \boxed{\sqrt{2}\,\rho\sigma\langle u \rangle} \quad [\tfrac{1}{\mathrm{s}}]$$



$$dL = \langle u \rangle dt$$

Mean Free Path and Number Density

Mean free path: average distance traveled between collisions:

$$l = \frac{\langle u \rangle}{Z_A} = \frac{\langle u \rangle}{\sqrt{2}\,\rho\sigma\langle u \rangle} = \frac{1}{\sqrt{2}\,\rho\sigma}$$

Define number density using ideal gas law:

$$PV = nRT \implies \frac{n}{V} = \frac{P}{RT}$$

$$\rho = \frac{N}{V} = \frac{nN_A}{V} = \left(\frac{P}{RT}\right) N_A$$

Substitute in number density $\boxed{\rho = \frac{N}{V} = \frac{PN_A}{RT}}$:

$$\boxed{l = \frac{RT}{\sqrt{2}\,N_A\sigma P} = \frac{V}{\sqrt{2}\,N\sigma}}$$

Note ρ is the *number density* (particles per unit volume), not molar concentration.

Total Collision Frequency Z_{AB}

Total Collision Frequency: total collisions per unit volume per unit time

Collision frequency for particle A in sea of B particles:

$$Z_{A(B)} = \rho\sigma\langle u_r\rangle = \sigma_{AB}\langle u_r\rangle\rho_B$$

Total collision frequency Z_{AB}, multiply by number density ρ_A:

$$Z_{AB} = \rho_A Z_{A(B)}$$

$$\boxed{Z_{AB} = \sigma_{AB}\langle u_r\rangle\rho_A\rho_B}$$

where $\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2$ and $\langle u_r\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$ with $\mu = \frac{m_Am_B}{m_A+m_B}$

Total Collision Frequency Z_{AA}

For identical particles (A colliding with A), $\rho_A = \rho_B = \rho$. Collision frequency:

$$Z_A = \sigma \langle u_r \rangle \rho$$

For identical particles, $\mu = \frac{m}{2}$, so the relative speed $\langle u_r \rangle = \sqrt{2}\langle u \rangle$:

$$Z_A = \sqrt{2}\rho\sigma\langle u \rangle$$

Total collision frequency Z_{AA} is $\rho \cdot Z_A$, but we double count collisions:

$$Z_{AA} = \frac{1}{2}\rho Z_A = \frac{1}{2}\rho\left(\sqrt{2}\rho\sigma\langle u \rangle\right)$$

$$\boxed{Z_{AA} = \frac{\sqrt{2}}{2}\rho^2\sigma\langle u \rangle}$$

Summary

Key Equations

Collision Frequency (collisions per particle per time)

$$Z_A = \sqrt{2}\,\rho\sigma\langle u\rangle \quad [\tfrac{1}{\mathrm{s}}]$$

Mean Free Path (dist. between collision)

$$l = \frac{RT}{\sqrt{2}\,N_A\sigma P} = \frac{V}{\sqrt{2}\,N\sigma}$$

Total collision frequency (total collisions per unit volume per unit time)

$$Z_{AB} = \sigma_{AB}\,\langle u_r\rangle\,\rho_A\rho_B$$

$$Z_{AA} = \frac{\sqrt{2}}{2}\rho^2\sigma\langle u\rangle$$

Helper Equations

Average and relative speed

$$\langle u\rangle = \sqrt{\frac{8k_BT}{\pi m}}$$

$$\langle u_r\rangle = \sqrt{2}\,\langle u\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

Reduced mass and cross-sections

$$\mu = \frac{m_Am_B}{m_A+m_B}$$

$$\sigma = \pi d^2$$

$$\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2$$

Number density

$$\rho = \frac{N}{V} = \frac{PN_A}{RT}$$

Example: Mean Free Path

Calculate the mean free path of a hydrogen molecule at standard conditions.

$$l = \frac{RT}{\sqrt{2}\, N_A \sigma P}$$

$$l = \frac{(0.0821\, \frac{\mathrm{L \cdot atm}}{\mathrm{mol \cdot K}})(273\,\mathrm{K})}{\sqrt{2} \cdot (6.022 \times 10^{23}\, \frac{1}{\mathrm{mol}}) \cdot (0.230 \times 10^{-18}\,\mathrm{m^2}) \cdot (1\,\mathrm{atm})}$$

$$l = \frac{22.41\,\mathrm{L}}{1.958 \times 10^{5}\,\mathrm{m^2}} \qquad \left(1\,\mathrm{L} = 10^{-3}\,\mathrm{m^3}\right)$$

$$l = 1.14 \times 10^{-7}\,\mathrm{m} = 114\,\mathrm{nm}$$

TABLE 27.3

Collision diameters, d(pm) and collision cross sections σ ($\mathrm{nm^2}$) for various molecules.

Gas	d/pm	$\sigma/\mathrm{nm^2}$
He	210	0.140
Ar	370	0.430
Xe	490	0.750
H_2	270	0.230
N_2	380	0.450
O_2	360	0.410
Cl_2	540	0.920
CH_4	410	0.530
C_2H_4	430	0.580

Example: Nitrogen Total Collision Frequency

Calculate the total collision frequency of N_2–N_2 in $1\,\mathrm{cm}^3$ of air (80% N_2) at standard conditions.

$$\rho = \frac{N_A P_{N_2}}{RT} = \frac{(6.022 \times 10^{23}\,\frac{1}{\mathrm{mol}})(0.80\,\mathrm{atm})}{(0.0821\,\frac{\mathrm{L\cdot atm}}{\mathrm{mol\cdot K}})(273\,\mathrm{K})}$$

$$= 2.15 \times 10^{25}\,\frac{1}{\mathrm{m}^3}$$

$$\langle u\rangle = \sqrt{\frac{8RT}{\pi M}} = 454\,\frac{\mathrm{m}}{\mathrm{s}}$$

Substituting into $Z_{AA} = \frac{\sqrt{2}}{2}\rho^2\sigma\langle u\rangle$:

$$Z_{N_2,N_2} = \frac{\sqrt{2}\,(2.15 \times 10^{25}\,\frac{1}{\mathrm{m}^3})^2(4.50 \times 10^{-19}\,\mathrm{m}^2)(454\,\frac{\mathrm{m}}{\mathrm{s}})}{2}$$

$$= 6.69 \times 10^{34}\,\frac{1}{\mathrm{s\cdot m}^3} = 6.69 \times 10^{28}\,\frac{1}{\mathrm{s\cdot cm}^3}$$

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Reaction Kinetics

At constant volume V, define molarity $[A] = n_A/V$:

$$\frac{d[A]}{dt} = \frac{1}{V}\frac{dn_A}{dt} = -\frac{\nu_A}{V}\frac{d\xi}{dt}$$
$$\frac{d[B]}{dt} = -\frac{\nu_B}{V}\frac{d\xi}{dt}$$
$$\frac{d[Y]}{dt} = \frac{\nu_Y}{V}\frac{d\xi}{dt}$$
$$\frac{d[Z]}{dt} = \frac{\nu_Z}{V}\frac{d\xi}{dt}$$

Define reaction rate:

$$v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

Example:

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$$

Simple Rate Laws

General reaction:

$$\nu_{\mathrm{A}}\,\mathrm{A} + \nu_{\mathrm{B}}\,\mathrm{B} \longrightarrow \nu_{\mathrm{Y}}\,\mathrm{Y} + \nu_{\mathrm{Z}}\,\mathrm{Z}$$

Empirical rate law:

$$v(t) = k[A]^m[B]^n$$

where

$$k: \text{ rate constant}$$
$$m, n: \text{ reaction orders (experimentally determined)}$$

$$\text{Overall order} = m + n$$

Units of the Rate Constant

Consider:

$$v = k[A]^1[B]^{1/2}$$

$$[v] = \frac{1}{\mathrm{s}} = M\,\mathrm{s}^{-1}$$
$$[A] = M, \quad [B] = M$$

So:

$$M\,\mathrm{s}^{-1} = k(M)^1(M)^{1/2} = kM^{3/2}$$

Solve for k:

$$k = M^{-1/2}\,\mathrm{s}^{-1}$$

Method of Initial Rates

Reaction:

$$2\,NO_2(g) + F_2(g) \longrightarrow 2\,NO_2F\,(g)$$

Assume:

$$v = k[NO_2]^m[F_2]^n$$

$$\frac{v_2}{v_1} = \left(\frac{[NO_2]_2}{[NO_2]_1}\right)^m$$

$$\ln\left(\frac{v_2}{v_1}\right) = m\ln\left(\frac{[NO_2]_2}{[NO_2]_1}\right)$$

$$\frac{v_3}{v_1} = \left(\frac{[F_2]_3}{[F_2]_1}\right)^n$$

$$\ln\left(\frac{v_3}{v_1}\right) = n\ln\left(\frac{[F_2]_3}{[F_2]_1}\right)$$

Determining k

Using:

$$v = k[NO_2]^m[F_2]^n$$

$$k = \frac{v}{[NO_2]^m[F_2]^n}$$

Substitute experimental values to obtain k, then:

$$v(t) = k[NO_2]^m[F_2]^n$$

First-Order Reactions

For:

$$\mathrm{A} \longrightarrow \text{products}$$

$$v(t) = -\frac{d[A]}{dt}$$

First-order rate law:

$$v(t) = k[A]$$

Equate:

$$-\frac{d[A]}{dt} = k[A]$$

Separate variables:

$$\frac{d[A]}{[A]} = -k\,dt$$

Integrated First-Order Rate Law

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

$$\ln[A] - \ln[A]_0 = -kt$$

Simplify:

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

Exponential form:

$$[A] = [A]_0 e^{-kt}$$