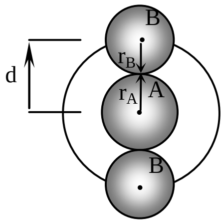
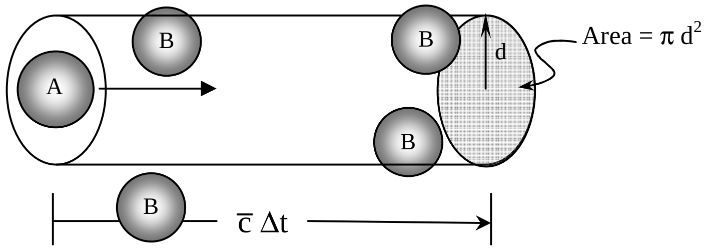
Collision Theory





$A + B \rightarrow$ products

N_A and N_B molecules in a container of volume V gives:
number densities of molecules: $\rho_A = N_A/V$ and $\rho_B = N_B/V$

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hard core collision cross section: $\sigma = \pi\,(r_A + r_B)^2 = \pi\, d^2$
d is the collision diameter

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molecule A moving, all others fixed:
in time Δt, A sweeps out volume $= \sigma\, \bar{c}\, \Delta t$

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number of molecules inside this volume $= \sigma\, \bar{c}\, \Delta t\, N_B/V$

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collision frequency = number of collisions per unit time $= \sigma\, \bar{c}\, N_B/V$

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total collisions $= N_A\, \sigma\, \bar{c}\, N_B/V$
total collisions per unit volume: $= \sigma\, \bar{c}\, (N_A/V)(N_B/V) = \sigma\, \bar{c}\, \rho_A\, \rho_B$

B molecules are moving: $z_{AB} = \sigma\, \bar{c}_{rel}\, (N_A/V)(N_B/V)$

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collisions per unit volume per unit time: $z_{AB} = \sigma \left(\frac{8kT}{\pi\mu}\right)^{1/2} \left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right)$ with $\mu = \frac{m_A\, m_B}{m_A + m_B}$

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reaction rate: $-\frac{d(N_A/V)}{dt} = z_{AB} = \sigma\, \bar{c}_{rel} \left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right)$ $[A] = \frac{1}{N_A}\left(\frac{N_A}{V}\right)$

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reaction rate: $-\frac{d(N_A/N_A V)}{dt} = z_{AB} = \sigma\, \bar{c}_{rel}\, N_A \left(\frac{N_A}{N_A V}\right)\left(\frac{N_B}{N_A V}\right)$

$$-\frac{d[A]}{dt} = z_{AB} = \sigma\, \bar{c}_{rel}\, N_A\, [A]\, [B]$$

$-\frac{d[A]}{dt} = k_2\, [A]\, [B]$ $k_2 = \sigma\, \bar{c}_{rel}\, N_A = \sigma \left(\frac{8kT}{\pi\mu}\right)^{1/2} N_A = \pi\, d^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} (1000\ \mathrm{L/m^3})\, N_A$

$H_2 + I_2 \rightarrow 2\, HI$ $r_{H_2} = 1.1$ Å $r_{I_2} = 1.7$ Å $\sigma = 0.246\ \mathrm{nm^2}$ $\bar{c}_{rel} = 2060\ \mathrm{m\ s^{-1}}$

$$k_2 = \pi\, (1.1\mathrm{x}10^{-10} + 1.7\mathrm{x}10^{-10}\mathrm{m})^2 \left(\frac{8(1.381\mathrm{x}10^{-23}\ \mathrm{J\ K^{-1}})(400\ \mathrm{K})}{\pi\ 3.33\mathrm{x}10^{-27}\ \mathrm{kg}}\right)^{1/2} (1000\ \mathrm{L/m^3})\ 6.022\mathrm{x}10^{23}\ \mathrm{mol^{-1}}$$
$$= 3.1\mathrm{x}10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$