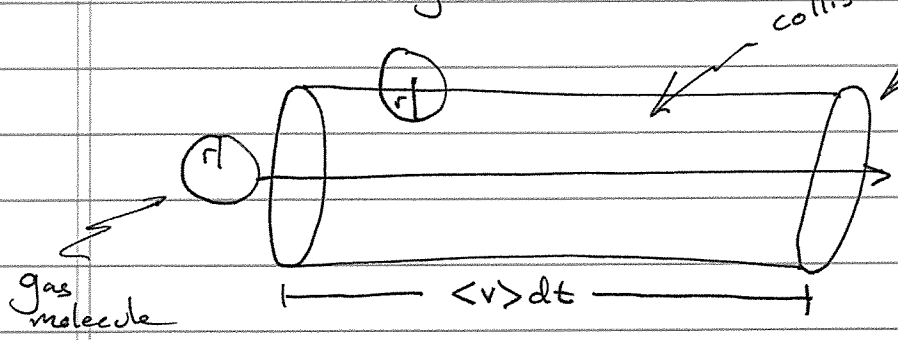
Last time we started talking about kinetics without realizing it:



$$\#\text{ of collisions} = \underbrace{\rho}_{\text{density of other particles}} \underbrace{\sigma}_{\text{collision cross section}} \underbrace{\langle v \rangle dt}_{\text{length of cylinder}} = dN_{coll}$$

Collision frequency $Z_A = \frac{dN_{coll}}{dt} = \rho\sigma\langle v \rangle \sqrt{2}$ ← correction for motion of other particles

$$= \sqrt{2}\rho\sigma\sqrt{\frac{8kT}{\pi M}}$$

That's the collision frequency for 1 particle.

The <u>total</u> collision frequency

$$Z_{AA} = \frac{1}{2}\rho Z_A$$

← the $\frac{1}{2}$ is to prevent counting collisions twice!

Σ "A" - "A" collisions

$$= \frac{\sigma\langle v \rangle \rho^2}{\sqrt{2}}$$

If we have 2 different <u>kinds</u> of molecules:

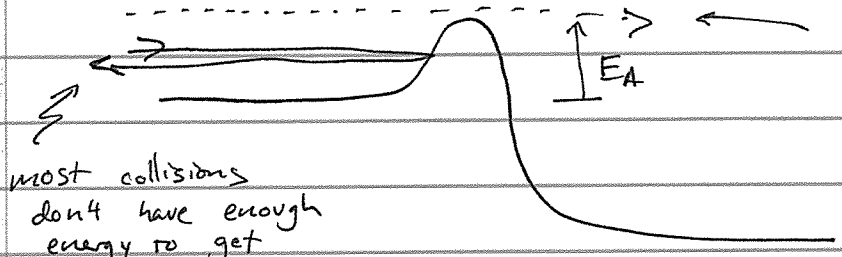
$$Z_{AB} = \sigma_{AB} \langle v_{rel} \rangle \rho_A \rho_B$$

with $\sigma_{AB} = \pi \left(\frac{d_A + d_B}{2} \right)^2$ $\quad \langle v_{rel} \rangle = \sqrt{\frac{8kT}{\pi \mu}}$

and $\mu = \frac{m_A m_B}{m_A + m_B}$ Generalized for dissimilar molecules!

In air, $Z_{N_2 N_2} \approx 6 \times 10^{28} \frac{1}{cm^3 \, s}$ ← that's a lot of collisions

Now let's consider a reaction: $A + BC \longrightarrow AB + C$



most collisions don't have enough energy to get over the barrier

only those which have a relative kinetic energy in excess of the activation energy (E_A) will react.

Remember: $Z_{AB} = \sigma_{AB} \rho_A \rho_B \underbrace{\langle v_{rel} \rangle}_{\int_0^\infty v_{rel} \, p(v_{rel}) \, dv_{rel}}$

Suppose we want to know how the collision frequency changes with increasing v_{rel}:

Start here: $P(v_{rel}) dv_{rel} = 4\pi \left(\frac{\mu}{2\pi kT} \right)^{3/2} v_{rel}^2 \, e^{-\mu v_{rel}^2 / 2kT} \, dv_{rel}$

$$dZ_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{\mu}{kT}\right)^{3/2} \frac{2}{\sqrt{\pi}} e^{-\mu v_{rel}^2/2kT} v_{rel}^3 \, dv_{rel}$$

- dZ_{AB}: change in # of AB collisions per unit volume
- $\sigma_{AB}\rho_A\rho_B \left(\frac{\mu}{kT}\right)^{3/2} \frac{2}{\sqrt{\pi}} e^{-\mu v_{rel}^2/2kT} v_{rel}^3 \, dv_{rel}$: # of AB collisions per unit volume per unit time with relative velocity between v_{rel} & $v_{rel} + dv_{rel}$
- dv_{rel}: change in relative speed

Now the relative kinetic energy: $KE = \frac{1}{2}\mu v_{rel}^2 = \epsilon_{rel}$

Let's change variables to ϵ_{rel}: $v_{rel} = \sqrt{\frac{2\epsilon_{rel}}{\mu}}$

$$dv_{rel} = \sqrt{\frac{1}{2\mu\epsilon_{rel}}} \, d\epsilon_{rel}$$

$\therefore$

$$dZ_{AB} = \sigma_{AB}\rho_A\rho_B \left(\frac{8}{\pi\mu}\right)^{1/2} \left(\frac{1}{k_B T}\right)^{3/2} \epsilon_{rel} e^{-\epsilon_{rel}/kT} \, d\epsilon_{rel}$$

And the number of collisions which have more energy that E_A:

$$\int_{E_A}^{\infty} dZ_{AB} = \sigma_{AB}\rho_A\rho_B \sqrt{\frac{8}{\pi\mu}} \left(\frac{1}{kT}\right)^{3/2} \int_{E_A}^{\infty} E e^{-E/kT} \, dE$$

$$Z_{AB}(E > E_A) = \sigma_{AB}\rho_A\rho_B \left(\frac{8kT}{\pi\mu}\right)^{1/2} \left(1 + \frac{E_A}{kT}\right) e^{-E_A/kT}$$

At large T this goes to $\propto e^{-E_A/kT}$

(Arrhenius rate law)!

The basic assumption of this model is that any binary collision of reactants that has enough energy to go over the activation barrier will do so

Since the concentrations: $[A] = \frac{n_A}{V} = \rho_A / N_{Avogadro}$ we've essentially described a 2nd order kinetic process:

$$A + BC \longrightarrow AB + C$$

$$\frac{d[A]}{dt} = -Z_{AB}(E > E_A)$$

$$= -k[A][BC] \quad \text{with}$$

$$\boxed{k = \sigma_{AB} N_A^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \left(1 + \frac{E_A}{RT}\right) e^{-E_A/RT}}$$

A general picture of reactions:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_Y Y + \nu_Z Z$$

$$n_A(t) = n_A(0) - \lambda \nu_A$$

(ν_A: stoichiometric constant; $n_A(t)$: moles of A @ time t; λ: reaction progress)

$$\frac{dn_A}{dt} = -\nu_A \frac{d\lambda}{dt}$$

$$n_Z(t) = n_Z(0) + \lambda \nu_Z$$

$$\frac{dn_Z}{dt} = \nu_Z \frac{d\lambda}{dt}$$

($\frac{dn_Z}{dt}$: rate of appearance of Z)

$$V(t) = \text{rate} = \frac{d\lambda}{dt}$$

A rate law ties the value of $V(t)$ to the concentrations at that time:

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$$

$$v(t) = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = k[NO]^2[O_2]$$

(k: rate constant)

Rate laws often have this form:

$$v(t) = k[A]^{m_A}[B]^{m_B}$$

(m_B: order of reaction in B; m_A: order of reaction in A)

Examples

$H_2 + I_2 \rightleftharpoons 2HI \qquad v(t) = k[H_2][I_2]$

$NO_2 + CO \rightarrow CO_2 + NO \qquad v(t) = k[NO_2]^2$

$Cl_2 + CO \rightleftharpoons Cl_2CO \qquad v(t) = k[Cl_2]^{3/2}[CO]$

Rate laws must be determined experimentally!

Elementary steps (often hidden by reaction expression) can govern the rate law via the rate limiting step:

$NO_2 + NO_2 \longrightarrow NO_2^* + NO_2$ ← excited NO_2 molecule

$NO_2^* + CO \rightleftharpoons CO_2 + NO$ ← only excited NO_2 can react

Elementary steps that explain rate laws are part of a mechanism for the reaction.

The Basic types:

$$A + B \longrightarrow C + D$$

1st order: $v(t) = k[A] = \frac{-d[A]}{dt}$ ← 1st order

diff eq is easy

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

$$\tau_{1/2} = \frac{\ln 2}{k}$$ ← half life of reaction, where $[A] = \frac{[A]_0}{2}$

0th order $A + M \longrightarrow B + M$

$v(t) = k$ ← no concentration dependence

$[A] = [A]_0 - kt$ (until all A is used up.)

0th order reactions are limited by reactive sites (e.g. catalysts & enzymes) If Liver alcohol dehydrogenase worked by 1st order:

$$EtOH \xrightarrow{LADH} CH_3 - C(=O) - H$$

$v(t) = -k[EtOH] \Longrightarrow [EtOH] = [EtOH]_0 e^{-kt}$

We would expect that 4x drinks would clear your body in only 3x the time as 1 drink

$1 \rightarrow \frac{1}{2} = 1\,\tau_{1/2}$

$4 \rightarrow 2 \rightarrow 1 \rightarrow \frac{1}{2} = 3\,\tau_{1/2}$

$8 \rightarrow 4 \rightarrow 2 \rightarrow 1 \rightarrow \frac{1}{2} = 4\,\tau_{1/2}$

(really 4 drinks takes 4x as long)