Lecture 33: Reaction Kinetics

Rate Law, Reaction Orders

Summary (corrected slide)

Key Equations

Collision Frequency (collisions per particle per time)

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

Mean Free Path (dist. between collision)

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

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

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

Reaction Rate

Consider a chemical reaction:

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

Use reaction coordinate $\xi(t)$ to write mols as function of time:

$$n_A(t) = n_{A,0} - \nu_A \xi(t)$$
$$n_B(t) = n_{B,0} - \nu_B \xi(t)$$
$$n_Y(t) = n_{Y,0} + \nu_Y \xi(t)$$
$$n_Z(t) = n_{Z,0} + \nu_Z \xi(t)$$

Take derivatives:

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt} \qquad \frac{dn_B}{dt} = -\nu_B \frac{d\xi}{dt} \qquad \frac{dn_Y}{dt} = \nu_Y \frac{d\xi}{dt} \qquad \frac{dn_Z}{dt} = \nu_Z \frac{d\xi}{dt}$$

Reaction Rate

At constant volume V, define molarity $[A] = \frac{n_A}{V}$ and substitute $\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt}$:

$$\frac{d[A]}{dt} = \frac{1}{V}\frac{dn_A}{dt} = -\frac{\nu_A}{V}\frac{d\xi}{dt}$$

$$\frac{d[B]}{dt} = -\frac{\nu_B}{V}\frac{d\xi}{dt} \qquad \frac{d[Y]}{dt} = \frac{\nu_Y}{V}\frac{d\xi}{dt} \qquad \frac{d[Z]}{dt} = \frac{\nu_Z}{V}\frac{d\xi}{dt}$$

Define reaction rate:

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

Example:

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

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

Empirical Rate Laws

Empirical Data: Used to determine rate law

Mechanisms: Must be consistent with rate law

Empirical Rate Law

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

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

$$k: \text{ rate constant}$$

$$m, n: \text{ reaction orders}$$

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

Units of the Rate Constant

Consider the following rate law:

$$rate = v(t) = k[A]^1[B]^{1/2}$$

Reaction rate is always in units of molarity per second

$$[v] = \frac{\mathrm{M}}{\mathrm{s}}$$
$$[A] = \mathrm{M}, \quad [B] = \mathrm{M}$$
$$\frac{\mathrm{M}}{\mathrm{s}} = k(\mathrm{M})^1(\mathrm{M})^{1/2}$$

Solve for k:

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

Important for when we move to complex reactions:

$$v(t) = \frac{k'[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k''[\mathrm{HBr}][\mathrm{Br_2}]^{-1}}$$

Method of Initial Rates

Reaction:

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

General form of rate law:

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

Run	$[NO_2]_0$	$[F_2]_0$	$v(t_0)$
1	1.15	1.15	6.12×10^{-4}
2	1.72	1.15	1.36×10^{-3}
3	1.15	2.30	1.22×10^{-3}

$$\frac{v_2}{v_1} = \frac{\cancel{k}[NO_2]_2^m \cancel{[F_2]_2^n}}{\cancel{k}[NO_2]_1^m \cancel{[F_2]_1^n}} = \left(\frac{[NO_2]_2}{[NO_2]_1}\right)^m$$

$$\frac{1.36 \times 10^{-3}}{6.12 \times 10^{-4}} = \left(\frac{1.72}{1.15}\right)^m \implies 2.22 = (1.496)^m$$

$$\ln(2.22) = m \ln(1.496) \implies m = 1.98$$

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

$$\frac{1.22 \times 10^{-3}}{6.12 \times 10^{-4}} = \left(\frac{2.30}{1.15}\right)^n \implies 1.993 = (2.00)^n$$

$$\ln(1.993) = n \ln(2.00) \implies n = 0.996$$

Method of Initial Rates

Reaction:

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

General form of rate law:

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

Run	$[NO_2]_0$	$[F_2]_0$	$v(t_0)$
1	1.15	1.15	6.12×10^{-4}
2	1.72	1.15	1.36×10^{-3}
3	1.15	2.30	1.22×10^{-3}

$$v(t) = k[NO_2]^2[F_2]^1$$

$$k = \frac{v(t)}{[NO_2]^2[F_2]} = \frac{6.12 \times 10^{-4}\ \frac{M}{s}}{(1.15\,M)^2(1.15\,M)}$$

$$= \frac{6.12 \times 10^{-4}\ \frac{M}{s}}{1.52\,M^3} = 4.02 \times 10^{-4}\ \frac{1}{M^2 \cdot s}$$

$$\boxed{v(t) = 4.02 \times 10^{-4}\ \frac{1}{M^2 \cdot s}[NO_2]^2[F_2]^1}$$

First order rate law

Consider a reaction:

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

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

First order rate law:

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

Set equal to eachother:

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

Separate variables and integrate:

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

Integrated First order Rate Law

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

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

Simplify:

$$\boxed{\ln \frac{[A]_t}{[A]_0} = -kt}$$

Equivalent exponential form:

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

Derivation of Integrated Rate Laws

Zero order

$$v(t) = -\frac{d[A]}{dt} = k$$
$$d[A] = -k\,dt$$
$$\int_{[A]_0}^{[A]_t} d[A] = -k\int_0^t dt$$
$$\boxed{[A]_t - [A]_0 = -kt}$$

Second order

$$v(t) = -\frac{d[A]}{dt} = k[A]^2$$
$$\frac{d[A]}{[A]^2} = -k\,dt$$
$$\int_{[A]_0}^{[A_t]} [A]^{-2}\,d[A] = -k\int_0^t dt$$
$$-\frac{1}{[A_t]} + \frac{1}{[A]_0} = -kt$$
$$\boxed{\frac{1}{[A_t]} = \frac{1}{[A]_0} + kt}$$

Summary of Reaction orders

The reaction kinetics formulas you actually need to know

	Zero order	**First order**	**Second order**
Differential rate law	$-\frac{d[A]}{dt} = k$	$-\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$
Integrated rate law	$[A]_t - [A]_0 = -kt$	$\ln\frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$
Solve for $[A]_t$	$[A]_t = -kt + [A]_0$	$[A]_t = [A]_0 e^{-kt}$	$[A]_t = \frac{[A]_0}{1 + [A]_0 kt}$