Foundations of Chemical Kinetics Lecture 8: Simple collision theory

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September 14, 2021

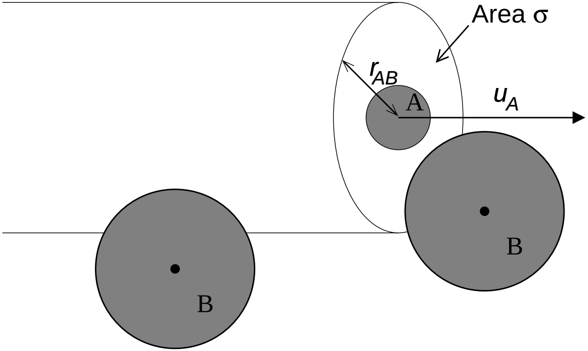
Simple collision theory

- In a gas-phase bimolecular reaction, the reactants have to meet in order to react.
- A very simple theory of bimolecular reactions might assume that reaction just requires a meeting with sufficient energy.
- A Boltzmann-Arrhenius factor takes care of the energy requirement.
- The collisional rate constant should thus yield an estimate of the preexponential factor.
- Alternatively, the collisional rate constant could give an upper limit on the preexponential factor and/or highlight cases with anomalously large preexponential factors.

Rate of collision

- Assume spherical molecules A and B of radii r_A and r_B. Define $r_{AB} = r_A + r_B$.
- Let n_A and n_B be the number of moles of A and B in the container.
- Imagine that the B molecules are stationary and focus on one A molecule.
- How many collisions with B molecules does A suffer per unit time?

Collision parameters



σ: collision cross-section

Number of collisions per unit time: number of B molecules whose centres lie within the volume swept out by the cross-section in unit time

Rate of collision (continued)

- Volume swept out by the cross-section per unit time: σu_A
- Number of B molecules per unit volume: $n_B L/V$
- Number of B molecules crossing cross-section per unit time: $(\sigma u_A)(n_B L/V) = \sigma u_A n_B L/V$ per molecule of A
- For $n_A L$ molecules, we get $n_A L(\sigma u_A n_B L/V) = \sigma u_A n_A n_B L^2/V$ collisions per unit time.
- To account for motion of B, replace u_A by the mean relative speed $\bar{u}_{\text{rel}}$.

  We want the rate of collisions per unit volume (since those are the usual units of rate of reaction), so divide by another factor of V.

  Rate of collisions:

$$Z_{AB} = \sigma \bar{u}_{\text{rel}} n_A n_B L^2/V^2$$

Collision theory rate constant

- Rate of reaction = (rate of collisions) × (Arrhenius factor)

$$v = Z_{AB} e^{-E_a/RT} = \sigma \bar{u}_{\text{rel}} L^2 \frac{n_A n_B}{V^2} e^{-E_a/RT}$$

- $[\text{A}] = n_A/V$ and $[\text{B}] = n_B/V$, so

$$v = \sigma \bar{u}_{\text{rel}} L^2 e^{-E_a/RT} [\text{A}][\text{B}]$$

- This rate is in molecules per unit volume per unit time. Divide by L to get the more customary units of moles per unit volume per unit time:

$$v = \sigma \bar{u}_{\text{rel}} L e^{-E_a/RT} [\text{A}][\text{B}]$$

Collision theory rate constant (continued)

$$u = \sigma \bar{u}_{\text{rel}} L e^{-E_a/RT} [\text{A}][\text{B}]$$

- The rate is in the mass-action form for a bimolecular reaction with

$$k_{\text{ct}} = \sigma \bar{u}_{\text{rel}} L e^{-E_a/RT}$$

and

$$A_{\text{ct}} = \sigma \bar{u}_{\text{rel}} L$$

A + A reactions

- For an A + A reaction, the method used above to count collisions would count every collision twice.

$$\therefore A_{\text{ct}} = \frac{1}{2}\sigma \bar{u}_{\text{rel}} L$$

- Also note that in this case $\mu = m_A/2$.

Example: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

Data: $A = 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}}$, $T = 500\,\mathrm{K}$

To do: Calculate cross-section assuming the reaction is collision-limited.

$$\mu_m = M_{\mathrm{HI}}/2 = \frac{127.908\,\mathrm{g\,mol^{-1}}}{2(1000\,\mathrm{g\,kg^{-1}})} = 6.3954 \times 10^{-2}\,\mathrm{kg\,mol^{-1}}$$

$$\bar{u}_{\mathrm{rel}} = \sqrt{\frac{8(8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}})(500\,\mathrm{K})}{\pi(6.3954 \times 10^{-2}\,\mathrm{kg/mol})}} = 407\,\mathrm{m/s}$$

$$\sigma = \frac{2A}{\bar{u}_{\mathrm{rel}}L} = \frac{2(10^{11}\,\mathrm{L\,mol^{-1}s^{-1}})}{(407\,\mathrm{m/s})(6.022\,142 \times 10^{23}\,\mathrm{mol^{-1}})(1000\,\mathrm{L\,m^{-3}})}$$
$$= 8 \times 10^{-19}\,\mathrm{m^2}$$

Example: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

(continued)

- Is this cross-section reasonable?
- Radius of the cross-section:

$$\sigma = \pi r_{AB}^2$$
$$\therefore r_{AB} = \sqrt{\sigma/\pi} = 5 \times 10^{-10}\,\text{m}$$

- Bond length in HI: $1.6092 \times 10^{-10}\,\text{m}$
- Is the reaction collision-limited?