Foundations of Chemical Kinetics

Lecture 8:
Simple collision theory

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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.
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

\[ \sigma: \text{collision cross-section} \]

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: $\sigma v_A$
- Number of B molecules per unit volume: $n_B L/V$
- Number of B molecules crossing cross-section per unit time: $(\sigma v_A)(n_B L/V) = \sigma v_A n_B L/V$ per molecule of A
- For $n_A L$ molecules, we get $n_A L(\sigma v_A n_B L/V) = \sigma v_A n_A n_B L^2/V$ collisions per unit time.
- To account for motion of B, replace $v_A$ by the mean relative speed $\bar{v}_r$.

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:

$$Z_{AB} = \sigma \bar{v}_r n_A n_B L^2/V^2$$
Mean relative speed

\[ \bar{v}_r = \sqrt{\frac{8k_B T}{\pi \mu}} = \sqrt{\frac{8RT}{\pi \mu_m}} \]

\[ \frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \]

\[ \frac{1}{\mu_m} = \frac{1}{M_A} + \frac{1}{M_B} \]
Collision theory rate constant

- Rate of reaction = (rate of collisions) $\times$ (Arrhenius factor)
  \[
  v = Z_{AB} e^{-E_a/RT} = \sigma \bar{v}_r L^2 \frac{n_A n_B}{V^2} e^{-E_a/RT}
  \]

- $[A] = n_A/V$ and $[B] = n_B/V$, so
  \[
  v = \sigma \bar{v}_r L^2 e^{-E_a/RT} [A][B]
  \]

- 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:
  \[
  v = \sigma \bar{v}_r L e^{-E_a/RT} [A][B]
  \]
Collision theory rate constant (continued)

\[ v = \sigma \bar{v}_r L e^{-E_a/RT} [A][B] \]

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

  \[ k_{ct} = \sigma \bar{v}_r L e^{-E_a/RT} \]

  and

  \[ A_{ct} = \sigma \bar{v}_r L \]
A + A reactions

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

\[ \therefore A_{ct} = \frac{1}{2} \sigma \bar{v}_r L \]

- Also note that in this case \( \mu = m_A/2 \).
Example: \(2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)\)

Data: \(A = 10^{11} \text{ L mol}^{-1} \text{s}^{-1}, \ T = 500 \text{ K}\)

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

\[
\mu_m = \frac{M_{\text{HI}}}{2} = \frac{127.908 \text{ g mol}^{-1}}{2(1000 \text{ g kg}^{-1})} = 6.3954 \times 10^{-2} \text{ kg mol}^{-1}
\]

\[
\bar{v}_r = \sqrt{\frac{8(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(500 \text{ K})}{\pi(6.3954 \times 10^{-2} \text{ kg/mol})}} = 407 \text{ m/s}
\]

\[
\sigma = \frac{2A}{\bar{v}_r L} = \frac{2(10^{11} \text{ L mol}^{-1} \text{s}^{-1})}{(407 \text{ m/s})(6.022142 \times 10^{23} \text{ mol}^{-1})(1000 \text{ L m}^{-3})} = 8 \times 10^{-19} \text{ m}^2
\]
Example: \[ 2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g) \]

(continued)

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

\[
\sigma = \pi r_{AB}^2
\]
\[
\therefore r_{AB} = \sqrt{\frac{\sigma}{\pi}} = 5 \times 10^{-10} \text{ m}
\]

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