

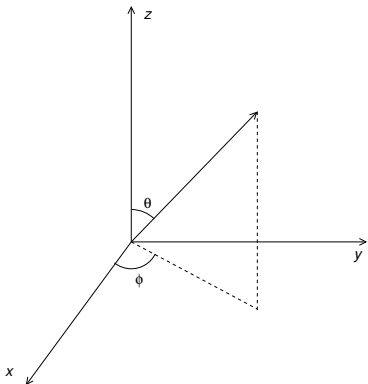
Foundations of Chemical Kinetics Lecture 5: Molecular beam experiments and Reactive scattering theory

Marc R. Roussel

September 18, 2021

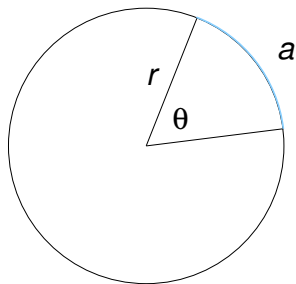
Some spherical geometry

Spherical polar coordinates



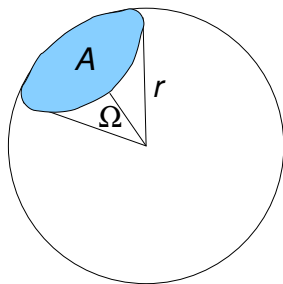
Some spherical geometry

Solid angles



$$\theta = a/r$$

unit: radians



$$\Omega = A/r^2$$

unit: steradians

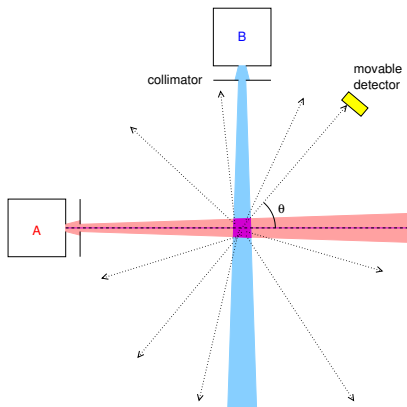
$$d\Omega = \sin \theta \, d\theta \, d\phi$$

Molecular-beam experiments

- Conventional chemical kinetics provides only crude information about a reaction, specifically the rate constant as a function of temperature.

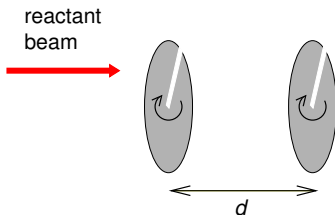
- Experimental chemical dynamics seeks to probe reactions on an elementary level in order to extract detailed information.

The basic experiment of chemical dynamics: Crossed molecular beams



Making a molecular beam

- Boil sample and heat gas to temperature T , then let it escape through a pinhole.
- Allow high-pressure gas to escape through a nozzle.
 - Adiabatic expansion through the nozzle makes a cold gas.
- The beam can be velocity selected using a pair of rotating disks.

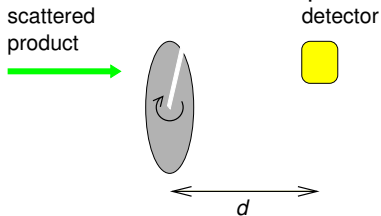


- Using lasers, the reactants can be excited to any desired quantum state prior to reaction.

Some detection methods

Mass spectrometry used for product identification

Time of flight measurement used for speed measurement



Some detection methods (continued)

Spectroscopy gives information on quantum state of product

Infrared chemiluminescence: Vibrationally excited products emit infrared photons as they relax to their ground vibrational state. The spectrum of this emission is analyzed to yield the distribution of quantum states of the product.

Laser induced fluorescence: A laser is tuned to a gap between two energy levels. The intensity of the subsequent fluorescence emission is proportional to the population of the initial state chosen, so again we get information on the distribution of quantum states of the product.

Data and insights obtained from molecular beam experiments

- Rate of product formation as a function of/resolved by
 - Reactant relative velocity
 - Reactant quantum state
 - Scattering angles
 - Product speed
 - Product quantum state

- In appropriately designed experiments, we get insight into where the energy goes after the products have been formed (rotation? vibration?) which in turn tells us something about the possible fate of those products in a more complex environment.

Reactive scattering

Moving on from simple collision theory

- In our previous treatment, we concentrated on the collision, and just assumed that the only other requirement for reaction was that the molecules have sufficient energy.
- In reactive scattering theory, we develop a theory that is inspired by experiments like molecular-beam experiments and consider the “before and after” of the reaction.
- We can consider more or less information about the initial quantum states of reactants, final quantum states of products, whether we consider the scattering angle, etc.
- We make no a priori assumption about the required energy for reaction.

The basic equation of reactive scattering theory

- Recall the simple collision theory rate:

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

- The basic equation of reactive scattering theory is, in differential form,

$$dv = L \left[\underbrace{I_R(\theta, \phi, u_{\text{rel}})}_{\substack{\text{differential cross-section} \\ d\sigma/d\Omega}} d\Omega \right] \left[\underbrace{u_{\text{rel}}p(u_{\text{rel}})du_{\text{rel}}}_{\substack{\text{relative speed weighted by the} \\ \text{Maxwell-Boltzmann distribution}}} \right] [A][B]$$

- Note: No explicit $e^{-E_a/RT}$ term, **but** $p(u_{\text{rel}})$ contains a Boltzmann factor and I_R depends on u_{rel} .

Reactive scattering (continued)

- Integrate to get the rate:

$$v = L \int \int \int I_R(\theta, \phi, u_{\text{rel}}) d\Omega u_{\text{rel}} \rho(u_{\text{rel}}) du_{\text{rel}} [A][B].$$

- $v = k[A][B]$ so

$$k = L \int \int \int I_R(\theta, \phi, u_{\text{rel}}) d\Omega u_{\text{rel}} \rho(u_{\text{rel}}) du_{\text{rel}}.$$

- Substitute in explicit form of $d\Omega$:

$$k = L \int_0^\infty \int_0^{2\pi} \int_0^\pi I_R(\theta, \phi, u_{\text{rel}}) u_{\text{rel}} \rho(u_{\text{rel}}) \sin \theta d\theta d\phi du_{\text{rel}}.$$

Reactive scattering (continued)

$$k = L \int_0^\infty \int_0^{2\pi} \int_0^\pi I_R(\theta, \phi, u_{\text{rel}}) u_{\text{rel}} \rho(u_{\text{rel}}) \sin \theta \, d\theta \, d\phi \, du_{\text{rel}}.$$

- We can integrate over the angular variables, since only I_R depends on them.

Define the **total cross-section**

$$\sigma_R(u_{\text{rel}}) = \int_0^{2\pi} \int_0^\pi I_R(\theta, \phi, u_{\text{rel}}) \sin \theta \, d\theta \, d\phi$$

$$\therefore k = L \int_0^\infty \sigma_R(u_{\text{rel}}) u_{\text{rel}} \rho(u_{\text{rel}}) \, du_{\text{rel}}$$

or
$$k = 4\pi L \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \int_0^\infty \sigma_R(u_{\text{rel}}) u_{\text{rel}}^2 \exp\left(\frac{-\mu u_{\text{rel}}^2}{2k_B T} \right) u_{\text{rel}} \, du_{\text{rel}}$$

Reactive scattering (continued)

$$k = 4\pi L \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \int_0^\infty \sigma_R(u_{\text{rel}}) u_{\text{rel}}^2 \exp\left(\frac{-\mu u_{\text{rel}}^2}{2k_B T} \right) u_{\text{rel}} du_{\text{rel}}$$

- We can rewrite this equation as an integral over kinetic energies.
- Relative kinetic energy:

$$\epsilon_k = \frac{1}{2} \mu u_{\text{rel}}^2$$

$$\therefore d\epsilon_k = \mu u_{\text{rel}} du_{\text{rel}}$$

- Substitute into k and get

$$k = \frac{L}{k_B T} \sqrt{\frac{8}{\pi \mu k_B T}} \int_0^\infty \epsilon_k \sigma_R(\epsilon_k) e^{-\epsilon_k/k_B T} d\epsilon_k$$

Example: Piecewise constant cross-section

- Suppose that the cross-section has the following (ideal gas/hard collider) form, with a cut-off to represent the activation energy:

$$\sigma_R(\epsilon_k) = \begin{cases} 0 & \text{for } \epsilon_k < \epsilon_a \\ \sigma & \text{for } \epsilon_k \geq \epsilon_a \end{cases}$$

- Then,

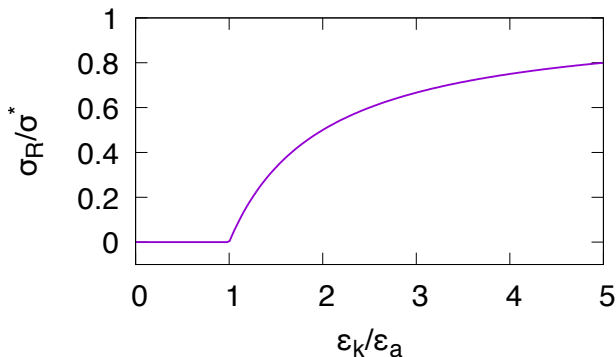
$$\begin{aligned} k &= \sigma \frac{L}{k_B T} \sqrt{\frac{8}{\pi \mu k_B T}} \int_{\epsilon_a}^{\infty} \epsilon_k e^{-\epsilon_k/k_B T} d\epsilon_k \\ &= \sigma L \sqrt{\frac{8}{\pi \mu k_B T}} (k_B T + \epsilon_a) e^{-\epsilon_a/k_B T} \\ \therefore A &= \sigma L \sqrt{\frac{8k_B T}{\pi \mu}} \left(1 + \frac{\epsilon_a}{k_B T} \right) \end{aligned}$$

- Looks like the simple collision theory result with a correction

Better example:

Cross-section goes continuously to zero at $\epsilon_k = \epsilon_a$

$$\sigma_R(\epsilon_k) = \begin{cases} 0 & \text{for } \epsilon_k < \epsilon_a \\ \sigma^* (1 - \epsilon_a/\epsilon_k) & \text{for } \epsilon_k \geq \epsilon_a \end{cases}$$



Better example:

Cross-section goes continuously to zero at $\epsilon_k = \epsilon_a$
(continued)

$$\begin{aligned}k &= \frac{L}{k_B T} \sqrt{\frac{8}{\pi \mu k_B T}} \int_{\epsilon_a}^{\infty} \epsilon_k \sigma^* (1 - \epsilon_a / \epsilon_k) e^{-\epsilon_k / k_B T} d\epsilon_k \\ &= \sigma^* L \sqrt{\frac{8 k_B T}{\pi \mu}} e^{-\epsilon_a / k_B T}\end{aligned}$$

⇒ agrees with simple collision theory

Generalizations

- So far, we have seen the differential and total cross-sections.

Differential cross-section:

- takes into account angular dependence of product distribution
- suitable for analyzing results of molecular-beam experiments

Total cross-section:

- averaged over all angles
 - suitable for understanding bulk kinetics
- The cross-section can also depend on the initial and final quantum states of the reactants and products. This is called a **state-to-state cross-section**.
 - State-to-state cross-sections are useful for advanced experiments in which the reactants are prepared in a specified state and the states of the products are analyzed by spectroscopy.