The Temperature Dependence of Rate Constants

CHEM 361A: Introduction to Physical Chemistry

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Lecture 16

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Learning Objective: Quantify how rate constants vary with temperature.

References:

- Atkins and de Paula Focus 6D
- Chang §12.5 and §12.7

Arrhenius Equation

19th century Swedish chemist Svante Arrhenius remarked that

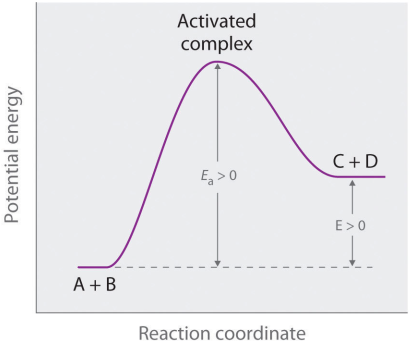
$$\ln k_f = intercept + slope \times \frac{1}{T}$$

This relationship is commonly expressed as the **Arrhenius Equation**:

$$k_f = Ae^{-E_a/RT}$$

Where

- A is the pre-exponential factor
- E_a is the activation energy of the reaction

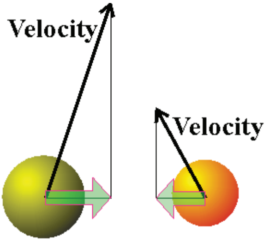


Collision Theory

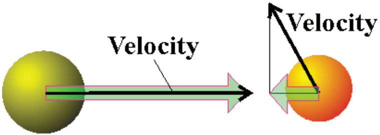
Collision Theory is based on the premise that

1. molecules must collide with the correct orientation
2. and sufficient energy along their line of approach

for a reaction to occur.



(a) Low kinetic energy of approach



(b) High kinetic energy of approach

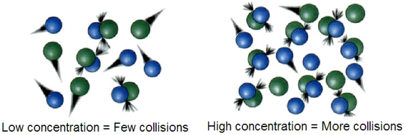
Collision Theory (cont.)

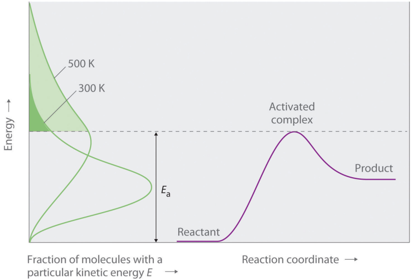
$$\text{rate} \propto \text{collision frequency} \times \text{fraction of collisions with } E_a$$

Collision Frequency $\propto$ [reactants]

Fraction of Collisions with Sufficient Energy:

$$f = e^{-E_a/RT}$$

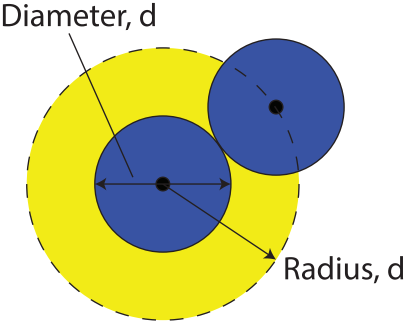




Interactive Demo

Collision Cross-Section

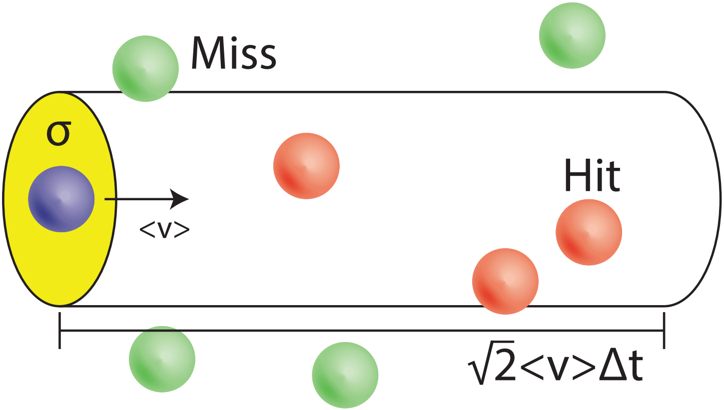
Collision Cross-Section, σ ($\mathbf{m^2}$): The target area presented by one molecule to another.



If the center one molecule comes within the yellow shaded area ($\sigma = \pi d^2$), then the molecules have collided.

Collision Frequency

The volume that one particle occupies over an interval of time is illustrated by



So the collision frequency depends on the number of other particles that occupy this same volume

Collision Frequency (cont.)

For a two molecule reaction, the collision frequency, Z_{AB}, between two molecules is

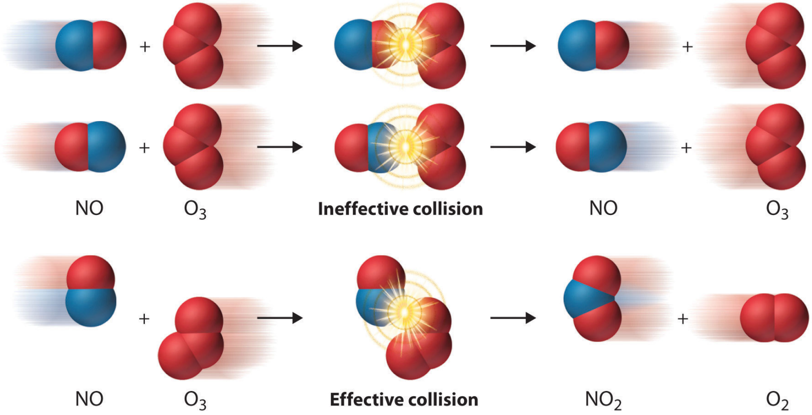
$$Z_{AB} = \underbrace{\sigma\sqrt{2}\langle v\rangle\Delta t}_{\text{Volume particle occupies}} \cdot \overbrace{[A][B]}^{\text{Density of particles}} \cdot \frac{1}{\underbrace{\Delta t}_{\text{per unit time}}} \cdot \overbrace{\frac{1}{2}}^{\text{Stops x2 counting}}$$

$$= \frac{\sigma\sqrt{2}\cancel{\Delta t}[A][B]}{2\cancel{\Delta t}}\sqrt{\frac{8k_BT}{\pi\mu}}; \quad \langle v\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

$$= \frac{\sigma\sqrt{2}[A][B]}{2}\sqrt{\frac{8k_BT}{\pi\mu}}; \quad \mu = \frac{m_Am_B}{m_A + m_B}$$

Steric Factor

Orientation of molecules is important. A steric factor, P, must be included in collision frequency



Value of P is only restricted to being greater than 0!

Collision Theory Summary

So for a reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{\mathrm{k_f}} \mathrm{P}$$

The second order rate law can be written as

$$\text{rate} = k_f[A][B] = \underbrace{\frac{P\sigma\sqrt{2}[A][B]}{2}\sqrt{\frac{8k_BT}{\pi\mu}}}_{\text{Collision Frequency}} \overbrace{e^{-E_a/RT}}^{\text{Fraction with Ea}}$$

This implies that

$$k_f = \underbrace{\frac{P\sigma\sqrt{2}}{2}\sqrt{\frac{8k_BT}{\pi\mu}}}_{\text{Arrhenius pre-factor, A}} e^{-E_a/RT}$$

Comparing to the Arrhenius Equation, the exponential pre-factor, A, can be interpreted as the collision frequency between molecules

Transition State Theory

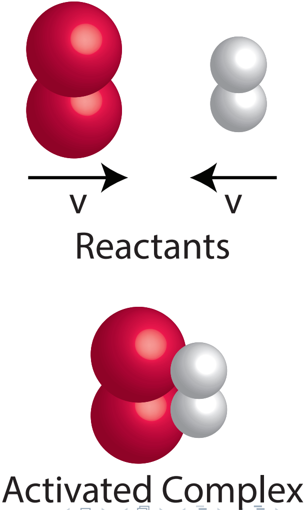
A more general theory, transition state theory, borrows from the notation of equilibrium

- Consider the reaction

  $$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}^{\ddagger}$$

  where $C^{\ddagger}$ is the activated complex.
- An equilibrium expression can be written as

  $$K^{\ddagger} = \frac{[C^{\ddagger}]}{[A][B]}$$



Eyring Equation

From this equilibrium it is possible to estimate the rate constant using the **Eyring equation**:

$$k_f = \kappa \frac{k_B T}{h} K^{\ddagger}$$

where

- κ is the transmission coefficient (the fraction of activated complexes that go to products). Unless otherwise stated, assume it is 1.
- k_B is Boltzmann's Constant ($1.38064852 \times 10^{-23}$ J K^{-1})
- h is Planck's Constant ($6.626070040 \times 10^{-34}$ J s)

Eyring Equation and Thermodynamics

It is more useful to express the Eyring equation using thermodynamic parameters. Recall that at equilibrium:

$$-RT\ln K = \Delta_r G^{\ominus}$$

The activation Gibbs Free Energy, $\Delta^{\ddagger}G$, will be used here:

$$-RT\ln K^{\ddagger} = \Delta^{\ddagger}G \quad \text{and} \quad K^{\ddagger} = e^{-\Delta^{\ddagger}G/RT}$$

Therefore, by writing

$$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S$$

we conclude that

$$k_f = \kappa\frac{k_B T}{h}e^{-(\Delta^{\ddagger}H - T\Delta^{\ddagger}S)/RT} = \overbrace{\left(\kappa\frac{k_B T}{h}e^{\Delta^{\ddagger}S/R}\right)}^{\text{Arrhenius pre-factor, A}} e^{-\Delta^{\ddagger}H/RT}$$

Back to Arrhenius

- Transition State Theory

$$k_f = \left(\kappa \frac{k_B T}{h} e^{\frac{\Delta^{\ddagger} S}{R}} \right) e^{-\frac{\Delta^{\ddagger} H}{RT}}$$

- Collision Theory

$$k_f = \left(\frac{P\sigma\sqrt{2}}{2} \sqrt{\frac{8 k_B T}{\pi\mu}} \right) e^{-\frac{E_a}{RT}}$$

- Arrhenius (Empirical)

$$k_f = A e^{-E_a/RT}$$

Remarkable that a complex series of events that both collision theory (gases) and transition state theory (gases and solutions) seek to characterise, displays Arrhenius-like behaviour.

Empirically Finding the Arrhenius Parameters

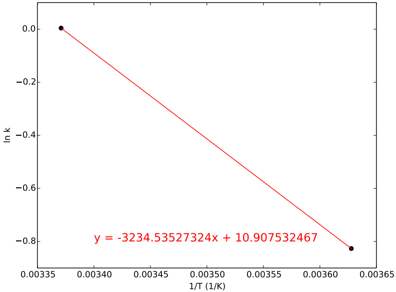
Methyl Orange is a pH indicator. Its decomposition in a tin/acid solution is a third order reaction

- rate $= \mathrm{k_f[MO][Sn^{2+}][H_3O^+]}$
- Arrhenius:

$$\ln k_f = \ln A - \frac{E_a}{RT}$$

- Data:

Temp (K)	k_f
296.65	1.004
275.65	0.4375



Determining the Arrhenius Parameters

Given that the fit to the Arrhenius equation

$$\ln k_f = \ln A - \frac{E_a}{RT}$$

is

$$y = -3234.5x + 10.91$$

determine the Activation Energy, E$_a$, and the pre-exponential factor A.

Finding the Rate Constant at a Different Temperature

Once the activation energy and the rate constant at one temperature is known, the rate constant can be found at a different temperature. Writing the Arrhenius equation at two different temperatures:

$$\ln k_f' = \ln A - \frac{E_a}{RT'} \quad \text{and} \quad \ln k_f = \ln A - \frac{E_a}{RT}$$

Then subtract the first from the second:

$$\ln k_f' - \ln k_f = -\frac{E_a}{RT'} + \frac{E_a}{RT}$$

Rearranging gives:

$$\ln k_f' - \ln k_f = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

Temperature Dependence of Rate Constants Example

Say you wanted to determine the rate of decomposition of Methyl Orange in your stomach if it were accidentally ingested. Assuming that it follows the same decomposition route ($E_a = 26.9$ kJ mol^{-1}), determine the rate constant at 37°C (k_f at 296.65 K is 1.004)

Summary

- The Arrhenius Equation is an empirical relationship relating the rate constant to temperature using the activation energy and an exponential pre-factor.

$$k_f = Ae^{-E_a/RT}$$

- The exponential pre-factor, A, is related to frequency at which reactants collide with the correct orientation. This can also be interpreted as being dependent on the thermal energy of the system and the change in entropy between the reactants and the activated complex.
- The activation energy, E_a is the difference in energy between the reactants and the activated complex.
- Finding the rate constant at a new temperature can be determined by

$$\ln k_f' - \ln k_f = \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$