Lecture Notes

Kinetics & Dynamics

Course CH-310

Fall 2024

Prof. Sascha Feldmann

Lectures: Wednesdays 1-3 pm, room MED 0 1418
Exercises: Wednesdays 3-4 pm, room MED 0 1418 & PH H3 31

Video recordings of the course from previous years

https://mediaspace.epfl.ch/channel/CH-310+Dynamics+and+Kinetics/29638

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Final exam

The written exam will take place during the exam period in January 2025, with a duration of 3 hours. You are allowed to bring a non-programmable calculator, as well as a formula sheet, which has to be A5 in size, single-sided, and hand-written.

Further reading

Atkins, P., de Paula, J., and Keeler. J. *Atkins' Physical Chemistry* (Oxford University Press, any edition).

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* (Prentice Hall, 1989).

McQuarrie, D. A. & Simon, J. D. *Physical Chemistry: A Molecular Approach* (University Science Books, 1997).

Laidler, K. J. *Chemical Kinetics* (Prentice Hall, 1987).

A big thank you to U. Lorenz and other previous lecturers, from whom this script has been adapted!

COURSE CONTENTS

Additional Content

Note: The additional content listed below is either beyond the scope of this Bachelor's level course or has already been covered by previous courses. It will not be examined, but you are welcome to read on it, if you are interested in learning more or benefit from a refresher, respectively. These contents occur in the lecture notes where they would naturally fit in in terms of content relation.

2.5 Exact Analytical Solution Methods
2.5.1 Matrix Method: Linear ODEs
2.5.2 Laplace Method: Linear ODEs
2.6 Numerical Solution Methods
2.6.1 Stochastic Method
2.6.2 Numerical Integration

5.6 An Application to Tolman's Theorem

7 Basic Concepts of Statistical Thermodynamics
7.1 Derivation of the Boltzmann Distribution
7.2 Partition Functions
7.3 Thermodynamic Functions
7.4 Equilibrium Constants of Gas Phase Reactions

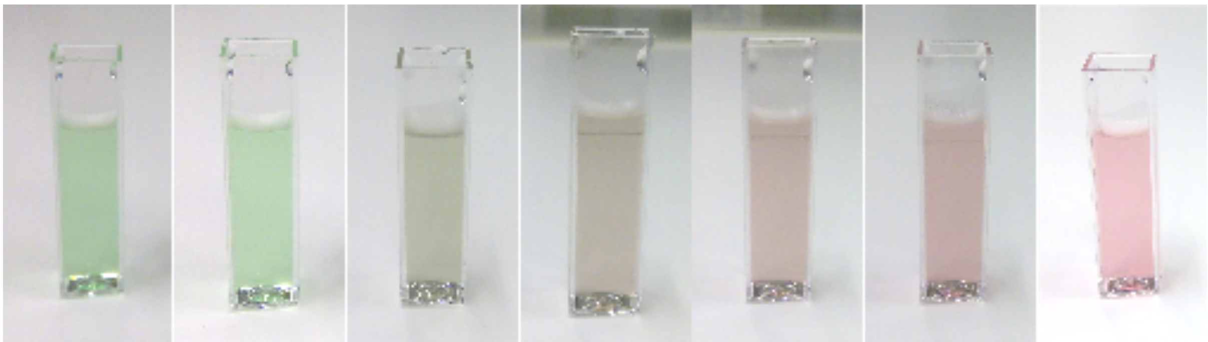
Appendix A – The Gamma Function

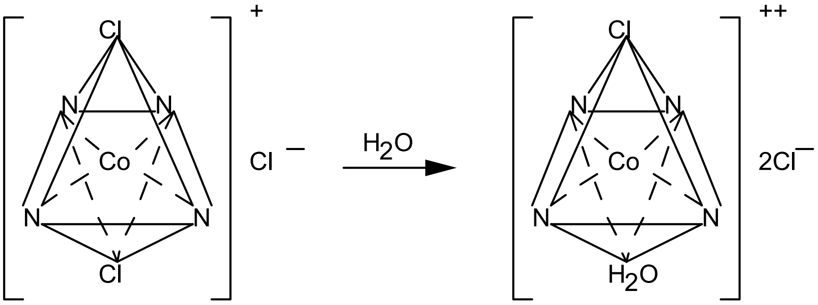
Appendix B – The Translational, Rotational, and Vibrational Partition Functions

1 BASIC CONCEPTS OF KINETICS

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 1. (Prentice Hall, 1989).

What is 'Chemical Kinetics'?





Chemistry

– the science of chemical compounds (composed of atoms) and their transformations

Phenomenological Thermodynamics

- equilibrium properties of matter
- concepts: Free Energy G, equilibrium constant K, …
- ensemble averaged properties

Macroscopic or Phenomenological Kinetics

- chemical transformations
- concepts: rate constant k, molecularity and order of a reaction
- ensemble averaged picture of reactions

Statistical Thermodynamics

- thermodynamics derived from an atomic/molecular picture

Microscopic Kinetics or Reaction Dynamics

- molecular origins of chemical reactions, reaction mechanisms

The chemical bond

Dynamics of the chemical bond

Quantum Mechanics

Time-independent Schrödinger equation

$$H\Psi = E\Psi$$

Time-dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial \mathrm{t}} = H\Psi$$

1.1 SOME DEFINITIONS

Chemical reactions can be *homogeneous* (occurring in only one phase) or *heterogeneous* (occurring in more than one phase).

Chemical reactions can be *irreversible*

$$2H_2 + O_2 \rightarrow 2H_2O$$

or *reversible*, i.e. having a *forward* and *reverse reaction*

$$H_2 + I_2 \rightleftarrows 2HI$$

Reactions occurring in a single step are called *elementary reactions*. The reaction of hydrogen and oxygen involves several of these *elementary reactions*, such as

$$O + H_2 \rightarrow OH + H$$

Reactions consisting of several such steps and therefore involving intermediates are called *complex*, *composite*, or *stepwise*. The reaction of hydrogen and oxygen is such a complex reaction.

For a stoichiometric equation

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

we can write down the rates for the consumption of the reactants or creation of the products

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

$$v_{\mathrm{C}} = \frac{d[\mathrm{C}]}{dt}$$

We define the rate of the reaction R as

$$R = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{c}\frac{d[\mathrm{C}]}{dt} = \frac{1}{d}\frac{d[\mathrm{D}]}{dt} = \frac{dx}{dt}$$

where R has units of [concentration/time]. Here, we have also defined the *extent of the reaction per unit volume* $x = \frac{[\mathrm{A}]-[\mathrm{A}]_0}{a} = \cdots$, where x has units of [concentration]. We assume that the volume is constant.

It is sometimes convenient to define the *extent of the reaction* $\xi = xV$ with

$$\xi = -\frac{1}{a}\big(n_{\mathrm{A}}(t) - n_{\mathrm{A}}(0)\big) = \frac{1}{c}\big(n_{\mathrm{C}}(t) - n_{\mathrm{C}}(0)\big) = \cdots$$

where n_{i} is the molar quantity of compound i and the *extent of the reaction* ξ has units of [mol]. Note that for constant volume

$$R = \frac{1}{V}\frac{d\xi}{dt}$$

1.2 ORDER AND MOLECULARITY OF A REACTION

We can distinguish *elementary* reactions based on their *molecularity*, *i.e.*, the number of reactants involved. Unimolecular reactions are for example decomposition reactions, like

$$\mathrm{N_2O_4 \rightarrow 2NO_2}$$

Bimolecular reactions involve two reactants, such as

$$\mathrm{O + H_2 \rightarrow OH + H}$$

Termolecular (trimolecular) reactions are for example encountered when a third collision partner is involved

$$\mathrm{A + B + M \rightarrow AB + M}$$

Reactions with four or more reactions are rare because of the low probability of four species colliding.

It is quite obvious that for an elementary bimolecular reaction, the rate of the reaction must be proportional to the concentration of both reactants, so that we obtain the *rate equation*

$$R = k[\mathrm{A}][\mathrm{B}]$$

where k is the *rate coefficient*.
More generally, one frequently finds that the experimental rate of a reaction is proportional to powers of the concentrations of different species involved. This allows us to write down an empirical *rate equation*, for example

$$R = k[\mathrm{A}]^m[\mathrm{B}]^n$$

and the powers m and n are the order of the reaction with respect to the species A and B, respectively. The overall *order* p of the reation is $p = m + n$. In general,

$$R = k\prod_i c_i^{n_i}$$

and

$$p = \sum_i n_i$$

The rate coefficient k has the units [concentration]$^{-(p-1)}$[time]$^{-1}$.

For elementary reactions, the order of the reaction is equal to the molecularity. However, for complex reactions, the orders are in general experimentally determined and may even be negative (inhibition) or fractional (indication of complex reaction). Moreover, the rate equation may not only contain the concentrations of reactants, but also those of products, intermediates, or other species involved, such as catalysts, and the rate equation may take a more complex mathematical form.

An example:

$$\mathrm{H_2 + Br_2 \rightarrow 2HBr}$$

$$\frac{d[\mathrm{HBr}]}{dt} = k[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}$$

And under different reaction conditions

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{1 + k'[\mathrm{HBr}]}$$

Here, the constants k and k' are phenomenological coefficients and should be referred to as *rate coefficients*, while the term *rate constant* is usually reserved for the coefficients in elementary reactions.

1.3 INTEGRATED REACTION RATE LAWS

By integrating the rate equation, which is an ordinary differential equation, we obtain the concentrations as a function of time.

1.3.1 ZERO-ORDER REACTIONS

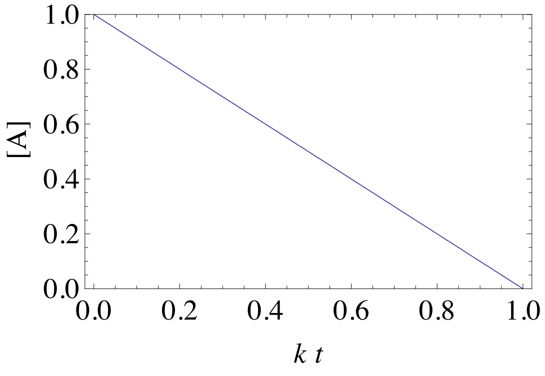
Zero-order reactions can be for example encountered for cases of heterogeneous catalysis on surfaces.

$$R = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^0 = k$$

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

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} d[\mathrm{A}] = -k \int_{t_0=0}^{t} dt$$

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - kt$$



1.3.2 FIRST-ORDER REACTIONS

Examples of first-order reactions are isomerizations, for example, the first-order unimolecular isomerization of methyl isocyanide

$$\mathrm{MeNC} \rightarrow \mathrm{MeCN}$$

$$\mathrm{A} \rightarrow \mathrm{B}$$

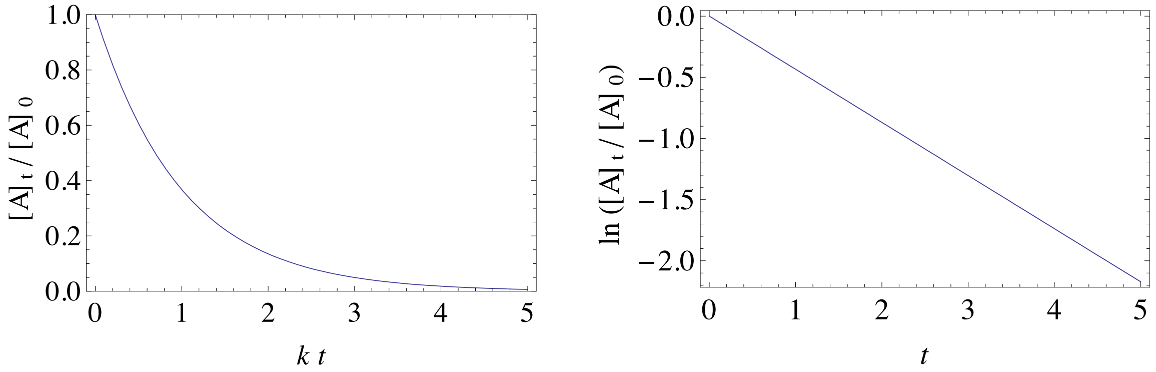
$$R = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^1$$

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

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]} = -k \int_{t_0=0}^{t} dt$$

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

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



We can define the *decay time* τ of the reaction

$$\tau = \frac{1}{k}$$

as well as the *half-life* $t_{\frac{1}{2}}$ at which $[\mathrm{A}]_{t_{\frac{1}{2}}} = \frac{1}{2}[\mathrm{A}]_0$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

1.3.3 SECOND-ORDER REACTIONS

First case: two identical reactants.

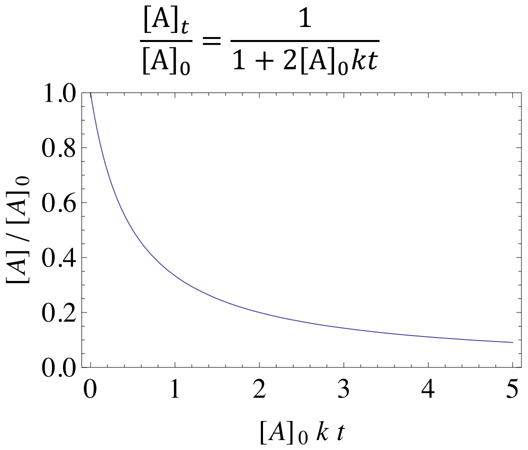
$$2\mathrm{A} \rightarrow \text{product(s)}$$

$$R = -\frac{1}{2}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^2$$

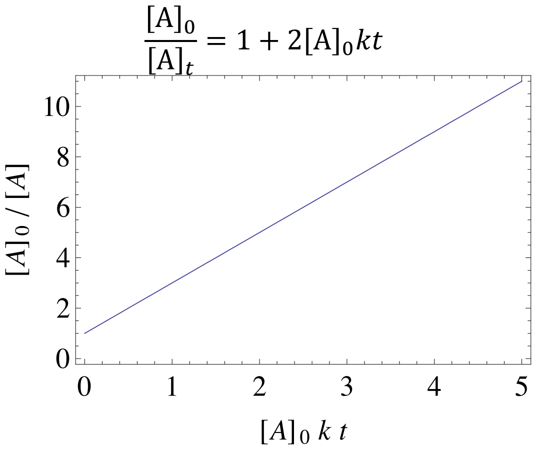
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -2k \int_{t_0=0}^{t} dt$$

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + 2kt$$

$$[\mathrm{A}]_t = \frac{[\mathrm{A}]_0}{1 + 2[\mathrm{A}]_0 kt}$$



$$\frac{[\mathrm{A}]_t}{[\mathrm{A}]_0} = \frac{1}{1 + 2[\mathrm{A}]_0 kt}$$



$$\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = 1 + 2[\mathrm{A}]_0 kt$$

Second case: two different reactants.

$$\mathrm{A+B} \rightarrow \text{product(s)}$$

$$R = \frac{dx}{dt} = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}] = k([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)$$

$$\int_0^{x_t} \frac{dx}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} = k \int_{t_0=0}^{t} dt$$

We solve the integral on the left by transforming the rational fraction of polynomials using the method of partial fractions. We set

$$\frac{1}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} = \frac{\alpha}{[\mathrm{A}]_0 - x} + \frac{\beta}{[\mathrm{B}]_0 - x}$$

$$\alpha([\mathrm{B}]_0 - x) + \beta([\mathrm{A}]_0 - x) = 1$$

and find

$$\alpha = -\beta = \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}$$

so that

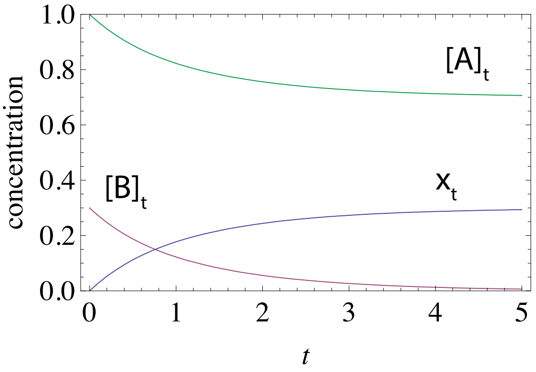
$$\int_0^{x_t} \frac{dx}{([\mathrm{A}]_0 - x)([\mathrm{B}]_0 - x)} = \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \left\{ \int_0^{x_t} \frac{dx}{x - [\mathrm{A}]_0} - \int_0^{x_t} \frac{dx}{x - [\mathrm{B}]_0} \right\}$$

$$= \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \ln \frac{([\mathrm{A}]_0 - x_t)[\mathrm{B}]_0}{([\mathrm{B}]_0 - x_t)[\mathrm{A}]_0}$$

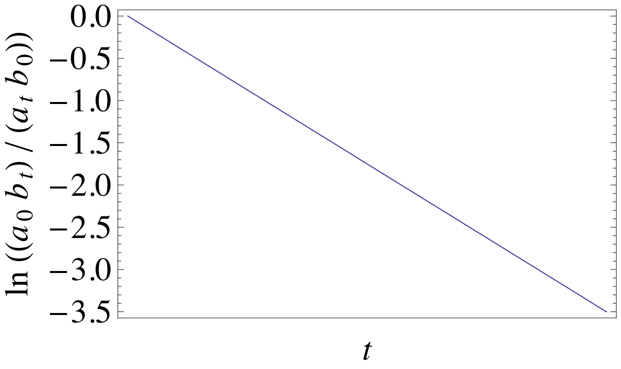
$$\frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \ln \frac{[\mathrm{A}]_t [\mathrm{B}]_0}{[\mathrm{B}]_t [\mathrm{A}]_0} = kt$$

$$x_t = \frac{[\mathrm{A}]_0 [\mathrm{B}]_0 \left(e^{[\mathrm{A}]_0 kt} - e^{[\mathrm{B}]_0 kt}\right)}{[\mathrm{A}]_0 e^{[\mathrm{A}]_0 kt} - [\mathrm{B}]_0 e^{[\mathrm{B}]_0 kt}}$$

$$x_t = \frac{[\mathrm{A}]_0 [\mathrm{B}]_0 \left(e^{[\mathrm{A}]_0 kt} - e^{[\mathrm{B}]_0 kt}\right)}{[\mathrm{A}]_0 e^{[\mathrm{A}]_0 kt} - [\mathrm{B}]_0 e^{[\mathrm{B}]_0 kt}}$$



$$\frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \ln \frac{[\mathrm{A}]_t [\mathrm{B}]_0}{[\mathrm{B}]_t [\mathrm{A}]_0} = kt$$



1.3.4 REACTIONS OF GENERAL ORDER

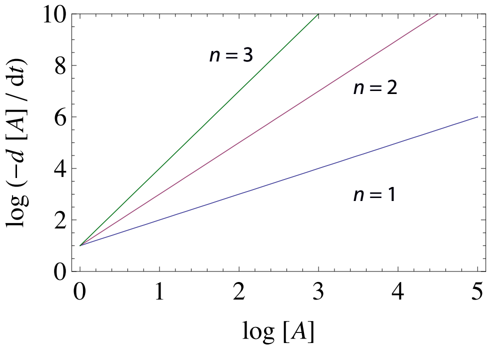
There are no known reactions of higher than third order. For completeness, we nevertheless develop the treatment for reactions that are of *n*th order in one reactant: $a\,\mathrm{A} \rightarrow \mathrm{product(s)}$

$$R = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]^n$$

$$\frac{1}{n-1}\left(\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) = akt$$

In order to deduce the order of a reaction, one can use a **van't Hoff plot**, a log-log plot of the rate equation, the slope of which gives the order n.

$$\ln\left(-\frac{d[\mathrm{A}]}{dt}\right) = n \ln[\mathrm{A}] + \ln ak$$



Note that it is also possible to plot the logarithm of the initial rate of disappearance $\ln\left(-\frac{d[\mathrm{A}]}{dt}\right)\Big|_{t=0}$ as a function of the logarithm of the initial concentration $\ln[A]_0$. In this case, several separate experiments are necessary.

The reaction order can also be determined by measuring reaction half-lives. We have already seen that for a first-order reaction the half-life $t_{\frac{1}{2}}$ is independent of the concentration of the reactant.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k}$$

As derived above, the integrated rate law for higher-order reactions is

$$\left(\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}}\right) = n(n-1)kt$$

Setting $[A]_t = \frac{1}{2}[A]_0$ and $t = t_{\frac{1}{2}}$, we obtain

$$t_{\frac{1}{2}} = \frac{(2^{n-1} - 1)}{n(n-1)k[A]_0^{n-1}}$$

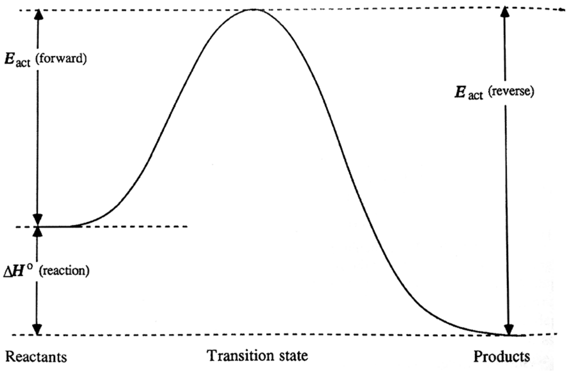
Thus, a log-log plot of the half-life $t_{\frac{1}{2}}$ versus the initial concentration $[A]_0$ gives a straight line with slope $-(n-1)$.

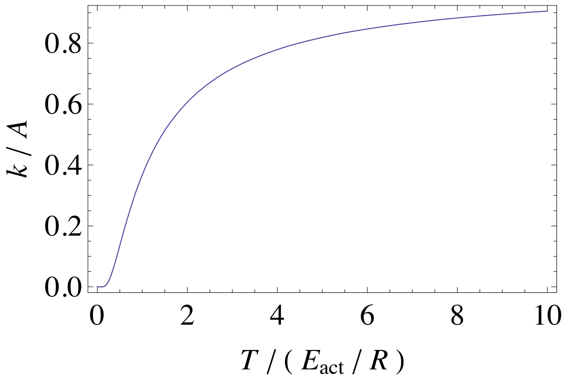
1.4 TEMPERATURE DEPENDENCE OF RATE CONSTANTS: THE ARRHENIUS EQUATION

The *Arrhenius equation* is an empirical expression for the dependence of a rate constant $k(T)$ on the absolute temperature T

$$k(T) = Ae^{-\frac{E_{\mathrm{act}}}{RT}}$$

Here, R is the ideal gas constant. The quantity A is called the *pre-exponential factor* or *frequency factor*, which may be slightly temperature-dependent. For a first-order reaction, A is has units of $[s^{-1}]$, and for a reaction of order p, its units are $\left[\text{concentration}^{-(p-1)}s^{-1}\right]$.
The activation energy E_{act} $[J\ mol^{-1}]$ can be thought of as the minimum amount of energy a reactant must possess to react.





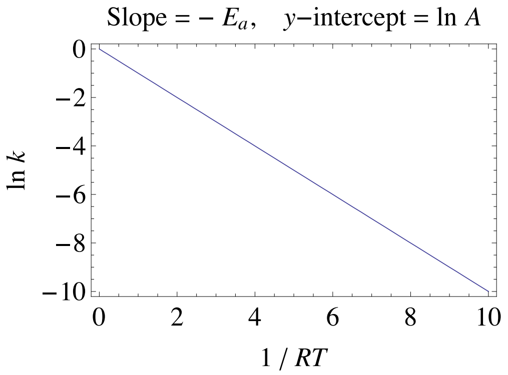
In fact, using a Boltzmann distribution, we find that the fraction of molecules with an energy larger than E_{act} is proportional to $e^{-\frac{E_{act}}{RT}}$. The activation energy is usually positive, but can be negative, for example if in a complex reaction, a weakly bound reactive intermediate is formed, such as in the recombination of iodine atoms.

$$\mathrm{I} + \mathrm{M} \rightarrow \mathrm{IM}$$

$$\mathrm{IM} + \mathrm{I} \rightarrow \mathrm{I}_2 + \mathrm{M}$$

The activation energy and prefactor can be obtained from an *Arrhenius plot* of $\ln k$ vs $1/\,T$.

$$\ln k = \ln A - \frac{E_{act}}{RT}$$



If we consider a forward and reverse reaction in equilibrium, we can relate the activation energy to a reaction enthalpy and the equilibrium constant, for example

$$\mathrm{A} + \mathrm{B} \underset{k_{\text{reverse}}}{\overset{k_{\text{forward}}}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$$

In equilibrium,

$$k_{\text{forward}}[\mathrm{A}][\mathrm{B}] = k_{\text{reverse}}[\mathrm{C}][\mathrm{D}]$$

$$K_{eq} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{A_{\text{forward}}}{A_{\text{reverse}}} e^{-\frac{(E_{\text{act, forward}} - E_{\text{act, reverse}})}{RT}} = \frac{A_{\text{forward}}}{A_{\text{reverse}}} e^{-\frac{\Delta H^0}{RT}}$$

2 COMPLEX REACTIONS

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 2. (Prentice Hall, 1989).

While in the previous chapter, we have mostly looked at simple elementary reactions, we will here study the kinetics of complex reactions. Our goal is always to find a solution to the (coupled) rate equations. From the integrated equations, we can then derive insights about the behavior of the reactive system.

We will also look at methods that frequently allow us to obtain approximate analytical solutions for complex reactions. Briefly, we will look at some analytical, as well as numerical tools for solving rate equations.

2.1 REVERSIBLE REACTIONS

In reversible reactions, a forward reaction leads to the formation of products, which can undergo a reverse reaction to reform the reactants. In the simplest case of a first-order reaction (*e.g.* cis-trans isomerization of dichloroehtylene)

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

we obtain two linear ODEs

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}]$$

We again use the extent of the reaction per unit volume $x = [\mathrm{A}]_0 - [\mathrm{A}] = [\mathrm{B}] - [\mathrm{B}]_0$ to simplify the description of the problem.

$$\frac{dx}{dt} = k_1([\mathrm{A}]_0 - x) - k_{-1}([\mathrm{B}]_0 + x) = -(k_1 + k_{-1})x + [k_1[\mathrm{A}]_0 - k_{-1}[\mathrm{B}]_0]$$

We substitute to simplify the expression

$$\frac{dx}{dt} = -kx + c$$

$$\int_0^{x_t} \frac{dx}{-kx + c} = \int_0^t dt$$

$$-\frac{1}{k}\int_0^{x_t} \frac{dx}{x - \frac{c}{k}} = -\frac{1}{k}\ln\left|\frac{x_t - \frac{c}{k}}{-\frac{c}{k}}\right| = t$$

We note that $\left(x_t - \frac{c}{k}\right) / \left(-\frac{c}{k}\right)$ is positive and thus find for the extent of the reaction per unit volume x_t

$$x_t = \frac{c}{k}(1 - e^{-kt})$$

We can see that for $t \to \infty$, x_t approaches an equilibrium value x_{eq} with

$$x_{\mathrm{eq}} = \lim_{t\to\infty} x_t = \frac{c}{k} = \frac{k_1[\mathrm{A}]_0 - k_{\text{-}1}[\mathrm{B}]_0}{(k_1 + k_{-1})}$$

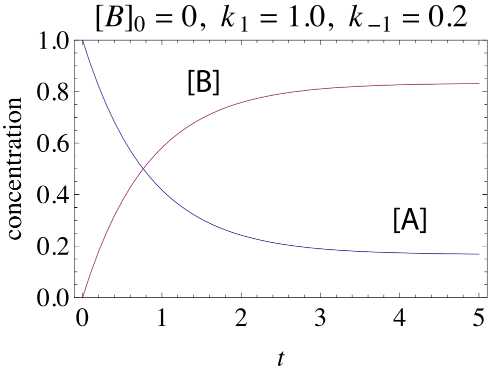
So that we can write

$$x_t = x_{\mathrm{eq}}(1 - e^{-kt})$$

We see that the extent of the reaction asymptotically approaches its equilibrium value x_{eq}. With $[\mathrm{A}]_{\mathrm{eq}} = [\mathrm{A}]_0 - x_{\mathrm{eq}}$ and $[\mathrm{B}]_{\mathrm{eq}} = [\mathrm{B}]_0 + x_{\mathrm{eq}}$, we can also write

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + x_{\mathrm{eq}} e^{-kt}$$

$$[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} - x_{\mathrm{eq}} e^{-kt}$$



We can relate the rate constants k_1 and k_{-1} to the equilibrium constant K_{eq} of the reversible reaction. In fact, we have already done so in section 1.4 for the Arrhenius rate constants of reversible reactions. In equilibrium, the principle of *detailed balance* must hold, *i.e.* the forward and reverse reaction must occur at the same rate

$$k_1[\mathrm{A}]_{\mathrm{eq}} = k_{\text{-}1}[\mathrm{B}]_{\mathrm{eq}}$$

so that

$$K_{\mathrm{eq}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_{\text{-}1}}$$

2.2 CONSECUTIVE REACTIONS

Consecutive reactions are sequential irreversible reactions. The following reaction sequence represents the simplest case of a first order consecutive reaction with two steps.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

An example is the radioactive decay of uranium to plutonium

$$^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu}$$

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}]$$

Compound A simply undergoes unimolecular decay.

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

By substituting into the equation for $d[\mathrm{B}]/dt$, we obtain

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-k_1 t} - k_2[\mathrm{B}]$$

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 e^{-k_1 t}$$

This is an inhomogeneous linear ODE, whose solution is the sum of the general solution of the homogeneous ODE and a particular solution of the inhomogeneous ODE.

For the general solution of the homogeneous ODE, we find

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = 0$$

$$[\mathrm{B}]_h = [\mathrm{B}]_{h,0} e^{-k_2 t}$$

where $[\mathrm{B}]_{h,0}$ is a free parameter, making this is a general solution.

We guess a particular solution for the inhomogeneous ODE, which we choose to contain the inhomogeneous term

$$[\mathrm{B}]_p = [\mathrm{B}]_{p,0} e^{-k_1 t}$$

In order to determine the constant $[\mathrm{B}]_{p,0}$, we subsitute into the inhomogeneous ODE

$$-k_1[\mathrm{B}]_{p,0} e^{-k_1 t} + k_2[\mathrm{B}]_{p,0} e^{-k_1 t} = k_1[\mathrm{A}]_0 e^{-k_1 t}$$

$$[\mathrm{B}]_{p,0} = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}$$

Finally, we add the general homogeneous and the particular inhomogeneous solutions.

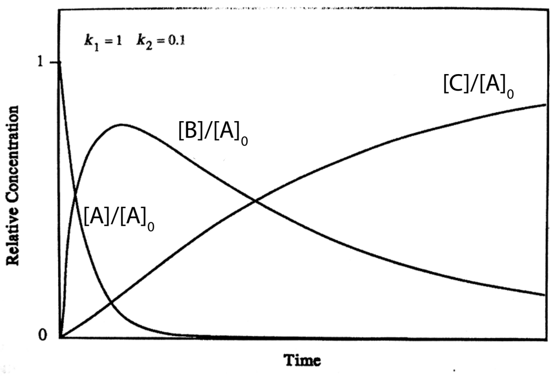
$$[\mathrm{B}] = [\mathrm{B}]_{h,0} e^{-k_2 t} + \frac{k_1[\mathrm{A}]_0}{k_2 - k_1} e^{-k_1 t}$$

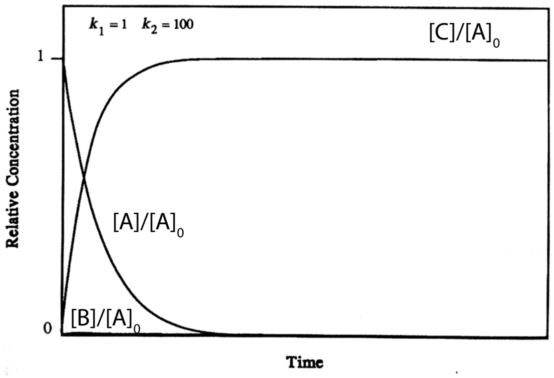
With the boundary conditions $[\mathrm{B}]_0 = [\mathrm{C}]_0 = 0$, we obtain

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

And with $[\mathrm{A}] + [\mathrm{B}] + [\mathrm{C}] = [\mathrm{A}]_0$, we find

$$[\mathrm{C}] = [\mathrm{A}]_0(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1})$$

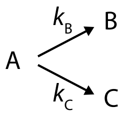




2.3 PARALLEL REACTIONS

In a parallel reaction, the same species participates in several different simultaneous processes. We will look at two simple examples.

First order decay to different products.



We can easily see that compound A decays with a first-order rate law.

$$[\mathrm{A}]_\mathrm{t} = [\mathrm{A}]_0 e^{-(k_\mathrm{B}+k_\mathrm{C})t}$$

$$\frac{d[\mathrm{B}]_\mathrm{t}}{dt} = k_\mathrm{B}[\mathrm{A}]_\mathrm{t} = k_\mathrm{B}[\mathrm{A}]_0 e^{-(k_\mathrm{B}+k_\mathrm{C})t}$$

With $[\mathrm{B}]_0 = [\mathrm{C}]_0 = 0$,

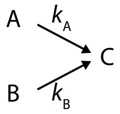
$$[\mathrm{B}]_\mathrm{t} = \frac{k_\mathrm{B}}{(k_\mathrm{B}+k_\mathrm{C})}[\mathrm{A}]_0(1 - e^{-(k_\mathrm{B}+k_\mathrm{C})t})$$

$$[\mathrm{C}]_\mathrm{t} = \frac{k_\mathrm{C}}{(k_\mathrm{B}+k_\mathrm{C})}[\mathrm{A}]_0(1 - e^{-(k_\mathrm{B}+k_\mathrm{C})t})$$

Note that the branching ratio $\frac{[\mathrm{B}]_\mathrm{t}}{[\mathrm{C}]_\mathrm{t}}$ is independent of time

$$\frac{[\mathrm{B}]_\mathrm{t}}{[\mathrm{C}]_\mathrm{t}} = \frac{k_\mathrm{B}}{k_\mathrm{C}}$$

First order decay to the same product.



Quiz: What are the integrate rate laws for this process?

2.4 APPROXIMATE SOLUTIONS TO COMPLEX REACTIONS

2.4.1 STEADY-STATE APPROXIMATION

For many complex reaction networks, analytic solutions cannot be obtained. However, by making suitable assumptions, one can sometimes find very useful approximate solutions that allow for good predictions. Such is the case for the steady-state approximation, which can be applied when intermediates A_i are present only in small quantities. In a set of coupled differential equations, the time derivative of this intermediate will be negligible compared with other time derivatives, so that we can approximate

$$\frac{d[\mathrm{A}_i]}{dt} \approx 0$$

Example 1. We will apply this approximation to the first order consecutive reaction with two steps that we already solved above.

$$\mathrm{A}\xrightarrow{k_1}\mathrm{B}\xrightarrow{k_2}\mathrm{C}$$

We assume that the concentration of the intermediate B under steady-state conditions $[\mathrm{B}]_\mathrm{S}$ is always small, which will be the case if $k_2 \gg k_1$, so that B reacts away faster than it is formed.

$$\frac{d[\mathrm{B}]_\mathrm{S}}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}]_\mathrm{S} = 0$$

$$[\mathrm{B}]_\mathrm{S} = \frac{k_1}{k_2}[\mathrm{A}] = \frac{k_1}{k_2}[\mathrm{A}]_0 e^{-k_1 t}$$

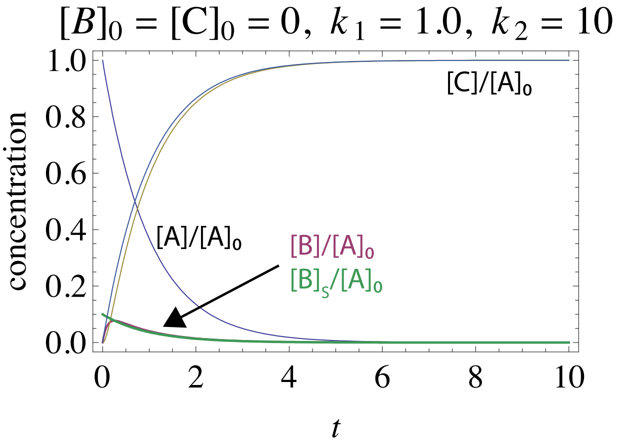
$$[\mathrm{C}] = [\mathrm{A}]_0(1 - e^{-k_1 t})$$

Note that we still find a time dependence for $[\mathrm{B}]_\mathrm{S}$, even though we assumed $\frac{d[\mathrm{B}]_\mathrm{S}}{dt} = 0$. We can however verify that $[\mathrm{B}]_\mathrm{S}/[\mathrm{A}] = \frac{k_1}{k_2} \ll 1$, which confirms our initial assumption that [B] is only present in small quantities. Product C builds up as if B was not present and we simply had a first order reaction $\mathrm{A}\xrightarrow{k_1}\mathrm{C}$.

Also note that the exact solution that we obtained above without making the steady-state approximation leads to the same result in the limit $k_2 \gg k_1$.

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \approx \frac{k_1}{k_2}[\mathrm{A}]_0 e^{-k_1 t}$$

$$[\mathrm{C}] = [\mathrm{A}]_0\left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right) \approx [\mathrm{A}]_0\left(1 - e^{-k_1 t}\right)$$



Example 2. A consecutive reaction with a reversible first step can be described by the following sequence.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B} \overset{k_2}{\rightarrow} \mathrm{C}$$

Such behavior is for example encountered in enzyme catalyzed reactions or thermally activated reactions. The rate equations are

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}]$$

While this problem can be solved analytically, we will here apply the steady-state approximation, assuming that [B] is small, so that

$$\frac{d[\mathrm{B}]_\mathrm{S}}{dt} = k_1[\mathrm{A}] - (k_{-1} + k_2)[\mathrm{B}]_\mathrm{S} = 0$$

$$[\mathrm{B}]_\mathrm{S} = \frac{k_1}{k_{-1} + k_2}[\mathrm{A}]$$

We can see that our approximation is only satisfied if $k_1 \ll k_{-1} + k_2$, *i.e.*, intermediate B reacts away much faster than it is formed and therefore has a small concentration. We find the other concentrations by substitution

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_{-1}[\mathrm{B}]_\mathrm{S} = \left(-k_1 + \frac{k_1 k_{-1}}{k_{-1} + k_2}\right)[\mathrm{A}] = -\frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{A}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}]_\mathrm{S} = \frac{k_1 k_2}{k_{-1} + k_2}[\mathrm{A}]$$

We see that the steady-state approximation leads to a simple first order reaction

$$\mathrm{A} \xrightarrow{k_\mathrm{eff}} \mathrm{C}$$

with $k_\mathrm{eff} = \frac{k_1 k_2}{k_{-1} + k_2}$.

Within our assumption that $k_1 \ll k_{-1} + k_2$, we can distinguish two limiting cases.

If $k_2 \gg k_{-1}$, then $k_\mathrm{eff} \approx k_1$ and the reaction effectively becomes $\mathrm{A} \xrightarrow{k_1} \mathrm{C}$. In this case, the first step of the sequence, $\mathrm{A} \xrightarrow{k_1} \mathrm{B}$ is the bottleneck of the reaction. We call this step *rate-limiting*, *rate-determining*, or *rate-controlling*.

If instead the second step $\mathrm{B} \xrightarrow{k_2} \mathrm{C}$ is rate-limiting, *i.e.* $k_{-1} \gg k_2$, then

$$k_\mathrm{eff} = \frac{k_1 k_2}{k_{-1}} = K k_2$$

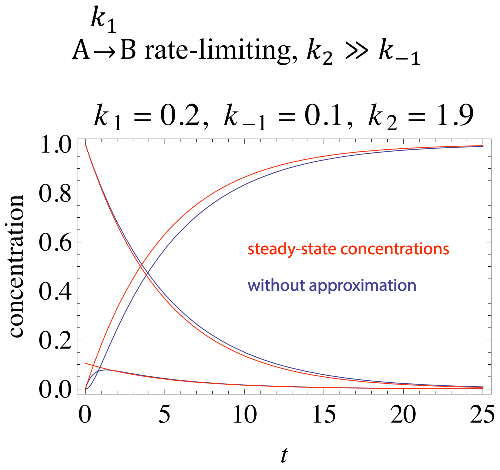
with $K = \frac{k_1}{k_{-1}}$. In this case, the second step is so slow that A and B are in a quasi-equilibrium

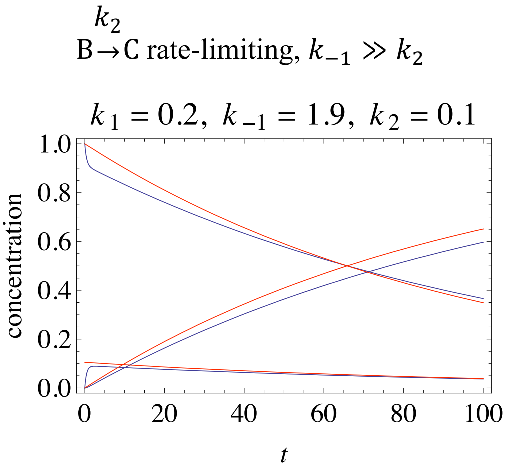
$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

with equilibrium constant $K = \frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_1}{k_{-1}}$. This quasi-equilibrium is called *pre-equilibrium*.

For the rate equation of C we find

$$\frac{d[\mathrm{C}]}{dt} = k_\mathrm{eff}[\mathrm{A}] = \frac{k_1 k_2}{k_{-1}}[\mathrm{A}] = K k_2[\mathrm{A}]$$





2.4.2 PSEUDO-FIRST-ORDER METHOD

The pseudo-first-order method is an experimental technique for simplifying the analysis of complex reactions involving several steps. It consists of *flooding* a reaction, *i.e.* supplying all reactants in excess except one, so that the reaction becomes pseudo-first-order in this one reactant.
Consider for example the competing reactions

$$\mathrm{A_1 + A_2 \xrightarrow{k_1} products}$$

$$\mathrm{A_1 + A_3 \xrightarrow{k_2} products}$$

with the second-order rate equations

$$\frac{d[\mathrm{A_2}]}{dt} = -k_1[\mathrm{A_1}][\mathrm{A_2}]$$

$$\frac{d[\mathrm{A_3}]}{dt} = -k_2[\mathrm{A_1}][\mathrm{A_3}]$$

If we supply $[\mathrm{A_1}]$ in large excess

$$[\mathrm{A_1}] \gg [\mathrm{A_2}] \text{ and } [\mathrm{A_1}] \gg [\mathrm{A_3}]$$

the concentration of $[\mathrm{A_1}]$ will remain almost constant over the course of the reaction

$$[\mathrm{A_1}] \approx \text{const.}$$

so that

$$\frac{d[\mathrm{A_2}]}{dt} = -k_1[\mathrm{A_1}][\mathrm{A_2}] \approx -\kappa_1[\mathrm{A_2}]$$

$$\frac{d[\mathrm{A_3}]}{dt} = -k_2[\mathrm{A_1}][\mathrm{A_3}] \approx -\kappa_2[\mathrm{A_3}]$$

We can see that the reactions become pseudo-first-order, making the complex reaction sequence simpler to analyze.

2.5 EXACT ANALYTICAL SOLUTION METHODS

2.5.1 MATRIX METHOD: LINEAR ODES

The matrix or determinant method is suitable for systems of linear ODEs, *i.e.* coupled differential equations of the type

$$\frac{d[\mathrm{A}_i]}{dt} = \sum_j k_{ij}[\mathrm{A}_j]$$

which we can rewrite as

$$\dot{a}_\iota = \sum_j k_{ij} a_j$$

Note that no terms a_j^n with $n > 1$ appear, nor any cross terms $a_j a_k$.

As an example, we will look again at the first order consecutive reaction with two steps

$$\mathrm{A}_1 \xrightarrow{k_1} \mathrm{A}_2 \xrightarrow{k_2} \mathrm{A}_3$$

We can write the coupled differential equations in matrix form as follows

$$\begin{pmatrix} \dot{a}_1 \\ \dot{a}_2 \\ \dot{a}_3 \end{pmatrix} = \begin{pmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}$$

or

$$\dot{\boldsymbol{a}} = \boldsymbol{Ma}$$

The idea of the matrix method is that this system of equations should be easier to solve in a different basis in which the matrix $\boldsymbol{M}$ containing the rate coefficients is diagonal. In that case, we obtain three independent first order rate equations that we know how to solve.

The diagonal matrix $\boldsymbol{\Lambda}$, is related to the matrix $\boldsymbol{M}$ through

$$\boldsymbol{MX} = \boldsymbol{X\Lambda}$$

$$\boldsymbol{X^{-1}MX} = \boldsymbol{\Lambda}$$

where $\boldsymbol{X}$ is a matrix, whose columns correspond to the eigenvectors $\boldsymbol{x_i}$ of $\boldsymbol{M}$, and $\boldsymbol{X^{-1}}$ is the inverse of $\boldsymbol{X}$. The diagonal elements of the matrix $\boldsymbol{\Lambda}$ are corresponding eigenvalues λ_i of $\boldsymbol{M}$. After transformation, we obtain

$$\boldsymbol{X^{-1}\dot{a}} = \boldsymbol{\Lambda\, X^{-1}a}$$

With $\boldsymbol{X^{-1}a} = \boldsymbol{a'}$, this becomes

$$\dot{\boldsymbol{a}'} = \boldsymbol{\Lambda a}'$$

Since $\boldsymbol{\Lambda}$ is diagonal, we end up with three independent first order equations

$$\dot{a_i'} = \lambda_i a_i'$$

with solutions

$$a_i' = c_i e^{\lambda_i t}$$

or

$$\boldsymbol{a}' = \begin{pmatrix} c_1 e^{\lambda_1 t} \\ c_2 e^{\lambda_2 t} \\ c_3 e^{\lambda_3 t} \end{pmatrix}$$

so that

$$\boldsymbol{a} = \boldsymbol{X} \begin{pmatrix} c_1 e^{\lambda_1 t} \\ c_2 e^{\lambda_2 t} \\ c_3 e^{\lambda_3 t} \end{pmatrix}$$

where the variables c_i are constants to be determined from the initial conditions.

We begin by finding the eigenvalues λ_i of $\boldsymbol{M}$.

$$|\boldsymbol{M} - \lambda \boldsymbol{I}| = 0$$

$$\begin{vmatrix} -k_1 - \lambda & 0 & 0 \\ k_1 & -k_2 - \lambda & 0 \\ 0 & k_2 & -\lambda \end{vmatrix} = (-k_1 - \lambda)(-k_2 - \lambda)(-\lambda) = 0$$

We obtain $\lambda_1 = -k_1$, $\lambda_2 = -k_2$, $\lambda_3 = 0$.

Next, we find the corresponding eigenvectors.

For $\lambda_1 = -k_1$

$$\begin{pmatrix} 0 & 0 & 0 \\ k_1 & k_1 - k_2 & 0 \\ 0 & k_2 & +k_1 \end{pmatrix} \begin{pmatrix} x_{1,1} \\ x_{1,2} \\ x_{1,3} \end{pmatrix} = 0$$

If we choose $x_{1,3} = 1$, we find $x_{1,2} = -k_1/k_2$, and $x_{1,1} = (k_1 - k_2)/k_2$, so that

$$\boldsymbol{x_1} = \begin{pmatrix} x_{1,1} \\ x_{1,2} \\ x_{1,3} \end{pmatrix} = \begin{pmatrix} (k_1 - k_2)/k_2 \\ -k_1/k_2 \\ 1 \end{pmatrix}$$

Similarly, we obtain

$$\boldsymbol{x_2} = \begin{pmatrix} 0 \\ -1 \\ 1 \end{pmatrix}$$

$$\boldsymbol{x_3} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

We obtain the matrix equation

$$\boldsymbol{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} (k_1 - k_2)/k_2 & 0 & 0 \\ -k_1/k_2 & -1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 e^{\lambda_1 t} \\ c_2 e^{\lambda_2 t} \\ c_3 e^{\lambda_3 t} \end{pmatrix}$$

In order to find the coefficients c_i, we impose the boundary condition $\boldsymbol{a}(t = 0) = \begin{pmatrix} a_{1,0} \\ 0 \\ 0 \end{pmatrix}$, so that

$$\begin{pmatrix} a_{1,0} \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} (k_1 - k_2)/k_2 & 0 & 0 \\ -k_1/k_2 & -1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}$$

We obtain

$$c_1 = \frac{k_2}{k_1 - k_2} a_{1,0}$$

$$c_2 = -\frac{k_1}{k_2} c_1 = \frac{k_1}{k_2 - k_1} a_{1,0}$$

$$c_3 = -c_1 - c_2 = a_{1,0}$$

This finally yields the time dependent concentrations $\boldsymbol{a}$

$$\boldsymbol{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} (k_1 - k_2)/k_2 & 0 & 0 \\ -k_1/k_2 & -1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 e^{\lambda_1 t} \\ c_2 e^{\lambda_2 t} \\ c_3 e^{\lambda_3 t} \end{pmatrix}$$

$$= \begin{pmatrix} (k_1 - k_2)/k_2 & 0 & 0 \\ -k_1/k_2 & -1 & 0 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} \frac{k_2}{k_1 - k_2} a_{1,0} e^{-\mathrm{k}_1 t} \\ \frac{k_1}{k_2 - k_1} a_{1,0} e^{-\mathrm{k}_2 t} \\ a_{1,0} \end{pmatrix}$$

$$= \begin{pmatrix} a_{1,0} e^{-\mathrm{k}_1 t} \\ a_{1,0} \frac{k_1}{k_2 - k_1} \left(e^{-\mathrm{k}_1 t} - e^{-\mathrm{k}_2 t}\right) \\ a_{1,0} \left\{1 + \frac{1}{k_2 - k_1} \left(k_1 e^{-\mathrm{k}_2 t} - k_2 e^{-\mathrm{k}_1 t}\right)\right\} \end{pmatrix}$$

Note that this agrees with the solution we found above.

2.5.2 LAPLACE METHOD: LINEAR ODES

(see the course “Numerical Methods”)

2.6 NUMERICAL SOLUTION METHODS

2.6.1 STOCHASTIC METHOD

The mathematical approach we have used so far for describing the kinetics of a system by a set of coupled differential equations is *deterministic*, *i.e.,* it allows us to predict the concentration of different species at any given point in time. However, we have not provided any justification for such an approach, other than that it seems to agree with experiments.

Here, we will put this procedure on a more solid foundation by looking at the reactions of individual molecules – an approach similar to that used in Statistical Thermodynamics. Because of the quantum nature of molecules and our lack of knowledge of the initial conditions of a molecule, we can regard its reaction as a *stochastic* process. We will find that in the limit of large numbers of molecules, a *stochastic description* of the reaction kinetics will frequently yield the same results as a deterministic description, if we consider *ensemble averages*. This is essentially a result of the law of large number.

However, a stochastic approach also allows us to describe *statistical fluctuations*, *i.e.* deviations from the mean. If these fluctuations, which we can quantify with the standard deviation, are small compared to the average value, a deterministic description is justified. However, if large fluctuations are present, so that the standard deviation is comparable to the average value, a deterministic approach may not yield a realistic description. Such is the case if strong correlations exist in the system. Fluctuations also dominate the behavior of a system if only a few reactants are present, such as a small number of enzymes in a cell.

Finally, the stochastic approach also offers a straightforward numerical recipe to solve complex differential equations, providing an alternative if numerical integration fails.

As an example, we will consider the irreversible reaction

$$\mathrm{A} \rightarrow \mathrm{B}$$

and assume that at $t = 0$, n_0 A molecules and no B molecules are present. At the core of the stochastic approach is the probability that one single A molecule will react to B within the next time period Δt:

$$p_{\text{reaction}} = 1 - e^{-k\Delta t} \approx k\Delta t$$

where k is a constant and where we have also assumed that Δt is sufficiently small. For n molecules of A, the probability $W_{n,n-1}(\Delta t)$ that any one of them will react within the next time period Δt is

$$W_{n,n-1}(\Delta t) = kn\Delta t + \mathcal{O}(\Delta t)$$

where the term $\mathcal{O}(\Delta t)$ describes the probability that more than one molecule will react. If we assume that Δt is small, this term will be negligible. Correspondingly, the probability $W_{n,n}(\Delta t)$ that no A molecule reacts is

$$W_{n,n}(\Delta t) = 1 - W_{n,n-1}(\Delta t) = 1 - \big(kn\Delta t + \mathcal{O}(\Delta t)\big)$$

We furthermore denote the probability of finding n molecules of A at time t as $P_n(t)$. For the probability $P_n(t + \Delta t)$ of finding n molecules at time $t + \Delta t$, we can then derive the expression

$$P_n(t + \Delta t) = P_{n+1}(t)W_{n+1,n}(\Delta t) + P_n(t)W_{n,n}(\Delta t)$$

which is a sum of the probability that $n + 1$ molecules were present at time t, of which one reacted, and the probability that only n molecules were present at time t, of which none reacted. In essence, this expression contains a sum over all the possible paths that lead to n molecules at time $t + \Delta t$. Upon substitution,

$$P_n(t + \Delta t) = k(n + 1)\Delta t P_{n+1}(t) + (1 - kn\Delta t)P_n(t) + \mathcal{O}(\Delta t)$$

rearrangement gives

$$\frac{P_n(t + \Delta t) - P_n(t)}{\Delta t} = k(n + 1)P_{n+1}(t) - knP_n(t) + \mathcal{O}(\Delta t)$$

which for $\Delta t \to 0$ becomes

$$\frac{dP_n}{dt} = k(n + 1)P_{n+1}(t) - knP_n(t)$$

This is called the *master equation* which describes the coupled rate equations for all possible states of the system. We will now try to find analytical solutions for all probabilities P_n, which will then allow us to make a connection to the deterministic description of the reaction.

The probability P_{n_0} can be easily found, since

$$P_{n_0+1}(t) = 0$$

so that

$$\frac{dP_{n_0}}{dt} = -kn_0P_{n_0}(t)$$

At time $t = 0$

$$P_{n_0}(t = 0) = 1$$

and we obtain

$$P_{n_0}(t) = e^{-kn_0t}$$

For the probability $P_{n_0-1}(t)$, $n = n_0 - 1$ and

$$\frac{dP_{n_0-1}}{dt} = kn_0e^{-kn_0t} - k(n_0 - 1)P_{n_0-1}(t)$$

To solve this inhomogeneous linear ODE, we first find a general solution of the homogeneous equation

$$P_{n_0-1} = ce^{-k(n_0-1)t}$$

Instead of guessing a particular solution of the inhomogeneous equation, as we have done above, we will here apply the *variation of constants*. We find the general solution of the inhomogeneous equation by setting

$$P_{n_0-1} = c(t)e^{-k(n_0-1)t}$$

which upon substitution into the inhomogeneous equation gives

$$\dot{c}(t)e^{-k(n_0-1)t} = kn_0 e^{-kn_0 t}$$

$$\dot{c}(t) = kn_0 e^{-kt}$$

$$c(t) = -n_0\left(e^{-kt} - 1\right) + c(0)$$

Since $P_{n_0-1}(0) = 0$, we can conclude that $c(0) = 0$, so that

$$P_{n_0-1} = n_0\left(1 - e^{-kt}\right)e^{-k(n_0-1)t}$$

We can rewrite this equation as follows

$$P_{n_0-1} = \binom{n_0}{n_0 - 1}\left(e^{-kt}\right)^{n_0-1}\left(1 - e^{-kt}\right)^{n_0-(n_0-1)}$$

This suggests the following interpretation. The term $\binom{n_0}{n_0 - 1}$ reflects the number of ways one can pick the $n_0 - 1$ unreacted molecules out of the total of n_0. The probability that one molecule has not reacted is e^{-kt}, so that the term $\left(e^{-kt}\right)^{n_0-1}$ is the probability that $n_0 - 1$ molecules have not done so. Finally, the term $\left(1 - e^{-kt}\right)^1$ is the probability for one molecule to have reacted.

Indeed, one can show that in general,

$$P_n = \binom{n_0}{n}\left(e^{-kt}\right)^n\left(1 - e^{-kt}\right)^{n_0-n}$$

which we can understand in a similar way. The probabilities P_n correspond in fact to a binomial distribution

$$P_n = \binom{n_0}{n}\left(e^{-kt}\right)^n\left(1 - e^{-kt}\right)^{n_0-n} = \binom{n_0}{n}p^n(1-p)^{n_0-n}$$

with $p = e^{-kt}$ the probability that a molecule has not reacted. In order to compare this distribution to the integrated rate equation as obtained from the deterministic approach, we calculate the mean number of molecules $\langle n(t)\rangle$ as well as the associated standard deviation $\sigma(t)$.

$$\langle n(t)\rangle = \sum_{n=0}^{n_0} nP_n = \sum_{n=0}^{n_0} n\binom{n_0}{n}p^n(1-p)^{n_0-n}$$

With

$$n\binom{n_0}{n} = n\frac{n_0!}{(n_0-n)!\,n!} = \frac{n_0(n_0-1)!}{(n_0-n)!\,(n-1)!} = n_0\binom{n_0-1}{n-1}$$

we find

$$\langle n(t)\rangle = n_0\sum_{n=1}^{n_0}\binom{n_0-1}{n-1}p^n(1-p)^{n_0-n} = n_0 p\sum_{n=1}^{n_0}\binom{n_0-1}{n-1}p^{n-1}(1-p)^{n_0-n}$$

Notice that the sum now runs from $n = 1$ to n_0. With $m = n - 1$ and $m_0 = n_0 - 1$

$$\langle n(t)\rangle = n_0 p \sum_{m=0}^{m_0} \binom{m_0}{m} p^m (1-p)^{m_0-m}$$

Since the sum over the entire distribution must equal one, we finally obtain

$$\langle n(t)\rangle = n_0 p = n_0 e^{-kt}$$

which is exactly the deterministic result. For the variance $\sigma(t)^2$, we find with a little more effort

$$\sigma(t)^2 = \sum_{n=0}^{n_0} (n - \langle n\rangle)^2 P_n = \sum_{n=0}^{n_0} n^2 P_n - \langle n\rangle^2 = n_0 e^{-kt}(1 - e^{-kt})$$

The ratio of the standard deviation and the average yields

$$\frac{\sigma(t)}{\langle n(t)\rangle} = \frac{\sqrt{e^{kt} - 1}}{\sqrt{n_0}}$$

showing that for large numbers of molecules n_0, the fluctuations will be small compared with the average value, in which case a deterministic approach is justified.

While we have here looked at the example of a simple reaction A → B, one can perform a similar analysis for more complex reactions. One always obtains the deterministic solution from the ensemble average. Whether such a deterministic description is justified or if instead fluctuations are important, can be decided based on the ratio of the standard deviation and the average value.

The stochastic approach also provides an alternative means of solving rate equations without having to resort to numerical integration. As an example, we will consider the reaction

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

The algorithm we will discuss here is based on generating random numbers in order to decide whether at a given point in time a molecule of A reacts to B or vice versa. In order to obtain an efficient algorithm, we divide the problem in two steps. First, we randomly pick a time τ at which the next reaction of either a molecule A or a molecule B will occur, while taking into account the probability distribution of reaction times $P(\tau)$. Then we randomly decide which of the two reactions takes place, according to the probabilities $P(i)$ for the reaction i to occur.

According to the discussion above, the probability $p_{\text{no reaction}}$ that no reaction of either the n_1 A molecules or the n_2 B molecules has occurred after time τ is

$$p_{\text{no reaction}} = e^{-(k_1 n_1 + k_2 n_2)\tau}$$

Consequently, the probability $P(\tau)d\tau$ for the reaction to occur in the time interval $[\tau, \tau + d\tau]$ must be proportional to the time derivative of the probability $p_{\text{no reaction}}$.

$$P(\tau)d\tau = -\frac{dp_{\text{no reaction}}}{d\tau} d\tau = (k_1 n_1 + k_2 n_2) e^{-(k_1 n_1 + k_2 n_2)\tau} d\tau = a e^{-a\tau} d\tau$$

with $a = \sum_i k_i n_i$. We can easily verify that the probability distribution $P(\tau)$ is normalized, *i.e.* $\int_0^\infty P(\tau)d\tau = 1$.

We use a random number generator to obtain a first random number r_1 in the interval $[0, 1]$ that will determine the reaction time τ, which we obtain from the cumulative probability for the reaction time is

$$P_{\text{cum}}(\tau) = \int_0^\tau P(\tau)d\tau = 1 - e^{-a\tau}$$

The random number r_1 replaces $P_{\text{cum}}(\tau)$, so that

$$\tau = \frac{1}{a}\ln\frac{1}{(1 - r_1)}$$

which produces the same result as

$$\tau = \frac{1}{a}\ln\frac{1}{r_1}$$

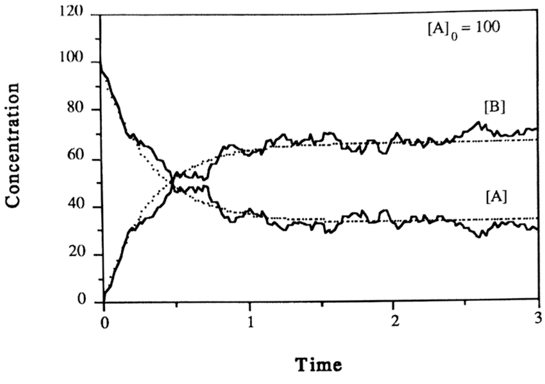
We then generate a second random number r_2 to decide which reaction i occurred at time τ. The probability $P(i)$ that reaction i occurs if any reaction occurs is then simply

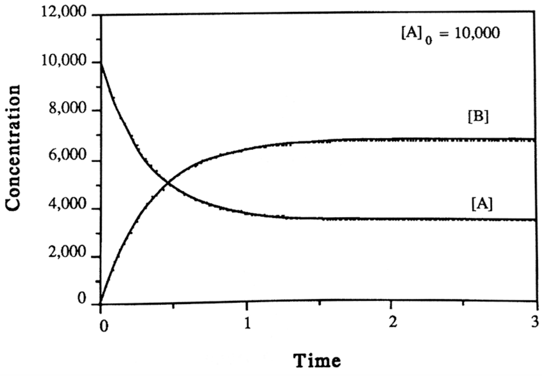
$$P(i) = \frac{k_i n_i}{\sum_i k_i n_i} = \frac{k_i n_i}{k_1 n_1 + k_2 n_2} = \frac{k_i n_i}{a}$$

so that

$$i = \begin{cases} 1 & \text{if } r_2 < k_1 n_1 / a \\ 2 & \text{if } r_2 > k_1 n_1 / a \end{cases}$$

We then increment the reaction time variable by τ and repeat the previous steps.





2.6.2 NUMERICAL INTEGRATION

(see the course "Numerical Methods")

3 CATALYSIS AND POLYMERIZATION

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 5. (Prentice Hall, 1989).

Atkins, P. & de Paula, J. *Atkins' Physical Chemistry* Ch. 20. (Oxford University Press, 2014).

3.1 CATALYSIS AND EQUILIBRIUM

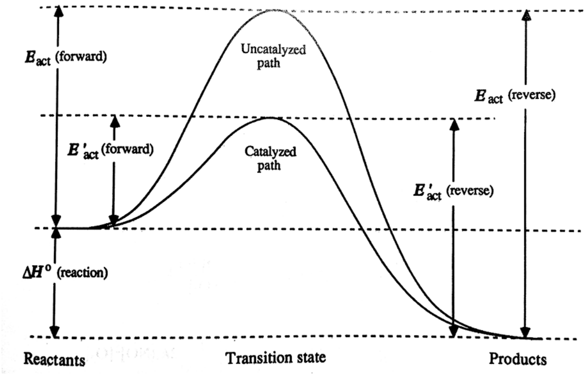
A catalyst is a chemical substance that increases the rate of a reaction without itself being consumed in the reaction. Formally, a reaction

$$\mathrm{A} \rightarrow \mathrm{B}$$

will proceed faster in the presence of a catalyst C

$$\mathrm{A} + \mathrm{C} \rightarrow \mathrm{B} + \mathrm{C}$$

The catalyst achieves this by lowering the activation energy of the reaction, without however changing the Free Energy of the reaction and therefore its equilibrium constant.



We can illustrate this for a reversible reaction at equilibrium

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$

for which a second catalyzed reaction path exists

$$\mathrm{A} + \mathrm{C} \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} \mathrm{B} + \mathrm{C}$$

According to the principle of detailed balance, we find at equilibrium

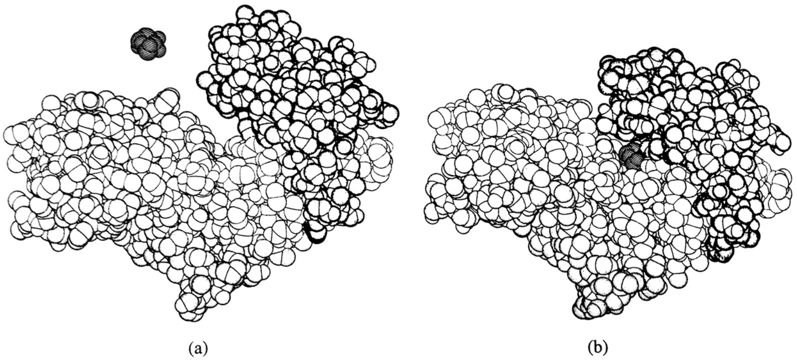
$$K'_{\mathrm{eq}} = \frac{k'_1}{k'_{-1}} = \frac{[B]_{\mathrm{eq}}[C]}{[A]_{\mathrm{eq}}[C]} = \frac{[B]_{\mathrm{eq}}}{[A]_{\mathrm{eq}}} = \frac{k_1}{k_{-1}} = K_{\mathrm{eq}}$$

We can conclude that the catalysts speeds both the forward and the reverse reaction up by the same factor.

3.2 ENZYMATIC CATALYSIS AND THE MICHAELIS-MENTEN MECHANISM

As an example, we will here look at enzymatically catalyzed reactions. Such reactions have in common that they proceed through an intermediate in which the substrate docks to the enzyme.

The figure below shows snapshots of such a process, illustrated with a space-filling model. A hexose docks to the active site of a hexokinase, which then catalyzes its phosphorylation. Subsequently, the reaction product is released.



In general, the reaction between enzyme E and substrate S

$$\mathrm{E} + \mathrm{S} \rightleftarrows \mathrm{ES} \rightleftarrows \mathrm{EZ} \rightleftarrows \mathrm{EP} \rightleftarrows \mathrm{E} + \mathrm{P}$$

will proceed through a number of intermediates, such as an enzyme-substrate complex (ES), an enzyme-product complex (EP), and an activated complex (EZ). The *Michaelis-Menten mechanism* simplifies this reaction sequence, which leads to a simple description of the kinetics that is useful for extracting various kinetic parameters.

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \overset{k_2}{\rightarrow} \mathrm{E} + \mathrm{P}$$

The assumptions are that

1) the reaction proceeds in only two steps,
2) there is no reverse reaction from the product(s) to the substrate (or we restrict our measurements to the initial stages of the reaction where $[\mathrm{P}]$ is small and the backreaction can be neglected).

Furthermore, in order to solve the resulting differential equations, we assume that

3) the steady-state approximation can be applied to the enzyme-substrate complex ES,
4) the enzyme concentration is much smaller than that of the substrate, $[\mathrm{E}] \ll [\mathrm{S}]$.

$$\frac{d[\mathrm{ES}]_\mathrm{S}}{dt} = k_1[\mathrm{E}][\mathrm{S}] - (k_{-1} + k_2)[\mathrm{ES}]_\mathrm{S} = 0$$

With $[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{ES}]_\mathrm{S}$, we obtain

$$[\mathrm{ES}]_\mathrm{S} = \frac{k_1[\mathrm{E}]_0[\mathrm{S}]}{k_1[\mathrm{S}] + k_{-1} + k_2}$$

Since $[\mathrm{ES}] \approx [\mathrm{E}] \ll [\mathrm{S}]$, we can approximate $[\mathrm{S}]_0 = [\mathrm{S}] + [\mathrm{P}]$, so that

$$v = -\frac{d[\mathrm{S}]}{dt} = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}]_\mathrm{S} = \frac{k_1 k_2 [\mathrm{E}]_0 [\mathrm{S}]}{k_1[\mathrm{S}] + k_{-1} + k_2}$$

which we can rewrite to obtain the *Michaelis-Menten Equation*:

$$v = \frac{k_2[\mathrm{E}]_0}{1 + \frac{k_{-1} + k_2}{k_1[\mathrm{S}]}} = \frac{v_\mathrm{max}}{1 + \frac{K_M}{[\mathrm{S}]}}$$

with the maximum rate $v_\mathrm{max} = k_2[\mathrm{E}]_0$ and the *Michaelis constant* $K_M = (k_{-1} + k_2)/k_1$.

We can distinguish two limiting cases. For $[\mathrm{S}] \ll K_M$,

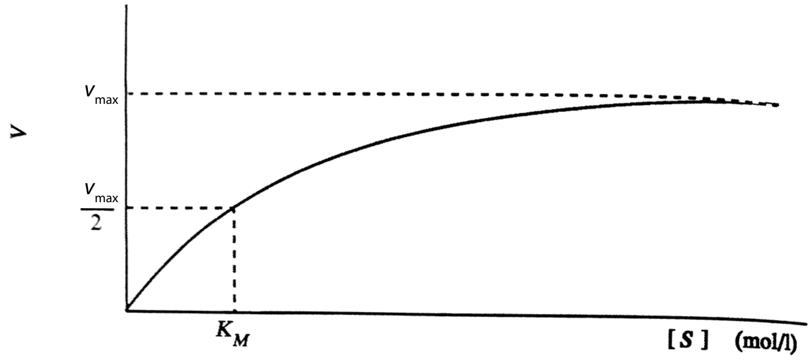
$$v = \frac{v_\mathrm{max}}{K_M}[\mathrm{S}] = \frac{k_2}{K_M}[\mathrm{E}]_0[\mathrm{S}]$$

so that the reaction becomes first-order in S. For $[\mathrm{S}] \gg K_M$,

$$v = v_\mathrm{max} = k_2[\mathrm{E}]_0$$

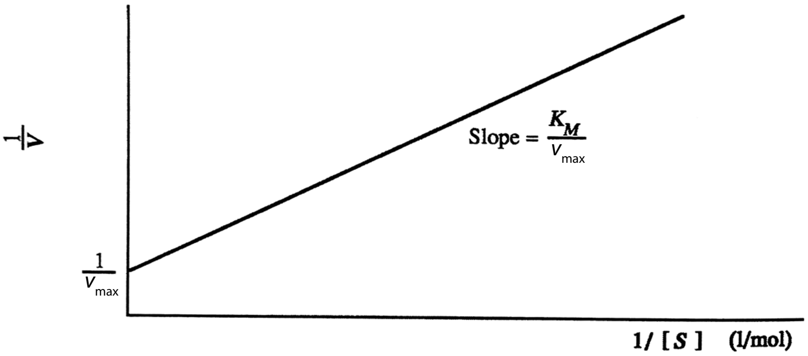
so that the reaction becomes zero-order in S. Under such conditions, the enzyme is essentially saturated due to the abundance of the substrate, and all the enzyme is tied up in the enzyme-substrate complex, *i.e.* $[\mathrm{ES}]_\mathrm{S} = [\mathrm{E}]_0$.

A plot of the rate v versus the substrate concentration [S] is called *Michaelis-Menten Plot*, from which one can obtain the maximum rate v_max as well as the *Michaelis constant* K_M:



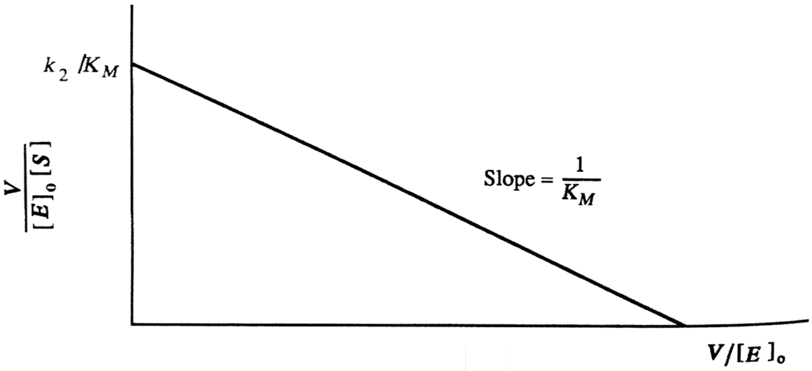
The *Lineweaver-Burk Plot* of $\frac{1}{v}$ versus $\frac{1}{[\mathrm{S}]}$ can afford better precision:

$$\frac{1}{v} = \frac{K_M}{v_\mathrm{max}}\frac{1}{[\mathrm{S}]} + \frac{1}{v_\mathrm{max}}$$



Another alternative is the *Eadie-Hofstee Plot*:

$$\frac{v}{[\mathrm{E}]_0[\mathrm{S}]} = \frac{k_2}{K_M} - \frac{v}{K_M[\mathrm{E}]_0}$$



3.3 INHIBITION OF ENZYMATIC REACTIONS

An inhibitor I decreases the rate of an enzyme catalyzed reaction, either by binding the enzyme E and thus leaving less free enzyme that can catalyze the reaction, or by binding to the enzyme-substrate complex ES and preventing the product formation from proceeding.

$$\begin{array}{ccccc} & k_1 & & k_2 & \\ \mathrm{E}+\mathrm{S} & \rightleftarrows & \mathrm{ES} & \rightarrow & \mathrm{E}+\mathrm{P} \\ & k_{-1} & & & \\ \uparrow\downarrow K_{\mathrm{EI}} & & \uparrow\downarrow K_{\mathrm{ESI}} & & \\ \mathrm{EI} & & \mathrm{ESI} & & \end{array}$$

In order to find an expression for the rate of product formation in the presence of an inhibitor, we apply the steady-state-approximation to the enzyme-substrate complex ES as above, so that

$$v = -\frac{d[\mathrm{S}]}{dt} = \frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ES}]_{\mathrm{S}}$$

Moreover, we also assume that the reaction ES $\xrightarrow{k_2}$ E + P is slow, so that all other species exist in a pre-equilibrium. In order to obtain an expression for $[\mathrm{ES}]_\mathrm{S}$, we write down the mass balance for the enzyme, as we did above:

$$[\mathrm{E}]_0 = [\mathrm{E}] + [\mathrm{EI}] + [\mathrm{ES}]_\mathrm{S} + [\mathrm{ESI}]$$

Under pre-equilibrium conditions, we can define the dissociation constants of the different complexes

$$K_\mathrm{ES} = \frac{k_{\text{-}1}}{k_1} = \frac{[\mathrm{E}][\mathrm{S}]}{[\mathrm{ES}]}; \quad K_\mathrm{EI} = \frac{[\mathrm{E}][\mathrm{I}]}{[\mathrm{EI}]}; \quad K_\mathrm{ESI} = \frac{[\mathrm{ES}][\mathrm{I}]}{[\mathrm{ESI}]}$$

so that we can substitute

$$[\mathrm{E}]_0 = [\mathrm{E}] + \frac{[\mathrm{E}][\mathrm{I}]}{K_\mathrm{EI}} + [\mathrm{ES}] + \frac{[\mathrm{ES}][\mathrm{I}]}{K_\mathrm{ESI}} = [\mathrm{E}]\alpha + [\mathrm{ES}]\alpha'$$

with

$$\alpha = 1 + \frac{[\mathrm{I}]}{K_\mathrm{EI}}; \quad \alpha' = 1 + \frac{[\mathrm{I}]}{K_\mathrm{ESI}}$$

We also substitute [E],

$$[\mathrm{E}]_0 = [\mathrm{ES}]\left(\alpha' + \alpha\frac{K_\mathrm{ES}}{[\mathrm{S}]}\right)$$

and finally obtain

$$v = k_2[\mathrm{ES}] = \frac{k_2[\mathrm{E}]_0}{\alpha' + \alpha\frac{K_\mathrm{ES}}{[\mathrm{S}]}} = \frac{v_\mathrm{max}}{\alpha' + \alpha\frac{K_\mathrm{ES}}{[\mathrm{S}]}}$$

This equation resembles the Michaelis-Menten equation

$$v_\mathrm{MM} = \frac{v_\mathrm{max}}{1 + \frac{K_M}{[\mathrm{S}]}}$$

which we obtain when we assume that no inhibition occurs, *i.e.*, the dissociation constants for the inhibitor become infinite, so that

$$\lim_{K_\mathrm{EI}\to\infty} \alpha = 1; \quad \lim_{K_\mathrm{ESI}\to\infty} \alpha' = 1$$

and

$$\lim_{\substack{K_\mathrm{EI}\to\infty,\\ K_\mathrm{ESI}\to\infty}} v = \frac{v_\mathrm{max}}{1 + \frac{K_\mathrm{ES}}{[\mathrm{S}]}}$$

By comparison,

$$K_M = \frac{k_{-1} + k_2}{k_1} \approx K_{\mathrm{ES}} = \frac{k_{-1}}{k_1}$$

which is the case, if $k_{-1} \gg k_2$. This is the condition for the existence of a pre-equilibrium as we assumed above.

We can distinguish three types of inhibition. **Competitive inhibition** occurs when the inhibitor binds to the active site of the enzyme, thus competing with the substrate

$$\mathrm{E + S} \overset{K_{\mathrm{ES}}}{\rightleftarrows} \mathrm{ES} \overset{k_2}{\rightarrow} \mathrm{E + P}$$

$$\uparrow\downarrow K_{\mathrm{EI}}$$

$$\mathrm{EI}$$

If no binding of the inhibitor to the enzyme-substrate complex ES occurs ($\alpha' = 1$ and $\alpha > 1$), so that

$$v = \frac{v_{\max}}{1 + \alpha \frac{K_{\mathrm{ES}}}{[\mathrm{S}]}}$$

We can see that at low concentrations of the substrate [S], the inhibitor slows down the reaction

$$v \approx \frac{v_{\max}}{\alpha K_{\mathrm{ES}}} [\mathrm{S}]$$

while in the limit of [S] → ∞, the maximum rate remains unchanged $v = v_{\max}$.

Uncompetitive inhibition occurs if the inhibitor prevents the enzyme-substrate complex ES from reacting to the products by binding to a site other than the active site.

$$\mathrm{E + S} \underset{k_{\text{-}1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \overset{k_2}{\rightarrow} \mathrm{E + P}$$

$$\uparrow\downarrow K_{\mathrm{ESI}}$$

$$\mathrm{ESI}$$

Without binding at the active site ($\alpha = 1$ and $\alpha' > 1$), so that

$$v = \frac{v_{\max}}{\alpha' + \frac{K_{\mathrm{ES}}}{[\mathrm{S}]}}$$

We can see that at low concentrations of the substrate [S], the inhibitor leaves the reaction rate unchanged

$$v \approx \frac{v_{\max}}{K_{\mathrm{ES}}} [\mathrm{S}]$$

while in the limit of [S] → ∞, the maximum rate is lowered $v = v_{\max}/\alpha'$.

Finally, for **mixed inhibition (noncompetitive inhibition)**, the inhibitor binds to both the enzyme E as well as the enzyme-substrate complex ES at a site other than the active site, so that $\alpha > 1$ and $\alpha' > 1$ and

$$v = \frac{v_{\max}}{\alpha' + \alpha \frac{K_{\mathrm{ES}}}{[\mathrm{S}]}}$$

In all cases, the efficiency of the inhibitor can be obtained through comparison of results from measurements in the presence and absence of the inhibitor.

3.4 AUTOCATALYSIS

Autocatalysis occurs when the product of a reaction appears as the reactant of either the same reaction or a coupled reaction. In the simplest case

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} 2\mathrm{B}$$

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

With the extent of the reaction per unit volume $x = [\mathrm{A}]_0 - [\mathrm{A}]_t = [\mathrm{B}]_t - [\mathrm{B}]_0$,

$$\frac{dx}{dt} = k([\mathrm{A}]_0 - x)(x + [\mathrm{B}]_0)$$

and

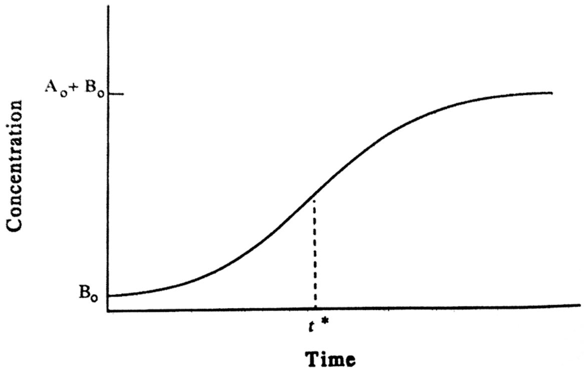
$$\int_0^x \frac{dx}{([\mathrm{A}]_0 - x)(x + [\mathrm{B}]_0)} = \int_0^t k dt$$

which we integrate with the method of partial fractions

$$\begin{aligned}\int_0^x \frac{dx}{([\mathrm{A}]_0 - x)(x + [\mathrm{B}]_0)} &= \frac{1}{[\mathrm{A}]_0 + [\mathrm{B}]_0}\left\{\int_0^x \frac{dx}{([\mathrm{A}]_0 - x)} + \int_0^x \frac{dx}{(x + [\mathrm{B}]_0)}\right\} \\ &= \frac{1}{[\mathrm{A}]_0 + [\mathrm{B}]_0} \ln\left|\frac{[A]_0(x + [B]_0)}{[B]_0([A]_0 - x)}\right| = kt\end{aligned}$$

With $[\mathrm{B}]_t = [\mathrm{B}]_0 + x$, we obtain

$$[\mathrm{B}]_t = \frac{[\mathrm{A}]_0 + [\mathrm{B}]_0}{1 + \frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} e^{-([\mathrm{A}]_0 + [\mathrm{B}]_0)kt}}$$



The time dependence of [B] shows a typical S curve: In the *induction period*, the rate of the reaction increases steadily, before it reaches a maximum at the *inflection point* at time t^*, after which the reaction rate slows until it drops to zero at long times. Such behavior is for example associated with the growth of a population, such as bacteria (B) with a limited food supply (A). Note that for an initial concentration $[\mathrm{B}]_0 = 0$, the reaction does not proceed.

3.5 POLYMERIZATION

We distinguish two cases of polymerization reactions.

In **stepwise polymerization**, any two monomers may react at any time or add to an already growing chain. An example is the polycondensation reaction of a hydroxyacid HO–R–COOH to form polyester:

$$\mathrm{HO{-}R{-}COOH} + \mathrm{HO{-}R{-}COOH} \rightarrow \mathrm{HO{-}R{-}COO{-}R{-}COOH} + \mathrm{H_2O}$$

The rate equation for the consumption of acid groups is

$$-\frac{d[\mathrm{A}]}{dt} = -\frac{d[\mathrm{COOH}]}{dt} = k[\mathrm{COOH}][\mathrm{OH}] = k[\mathrm{A}]^2$$

where we have used that $[\mathrm{COOH}] = [\mathrm{OH}] = [\mathrm{A}]$. As we have derived above,

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + kt[\mathrm{A}]_0}$$

The fraction p of monomers that have reacted is

$$p = \frac{[\mathrm{A}]_0 - [\mathrm{A}]}{[\mathrm{A}]_0} = \frac{kt[\mathrm{A}]_0}{1 + kt[\mathrm{A}]_0}$$

and the *degree of polymerization*, *i.e.*, the average chain length $\langle N \rangle$ is

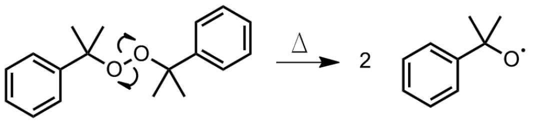
$$\langle N \rangle = \frac{[\mathrm{A}]_0}{[\mathrm{A}]} = \frac{1}{1-p} = 1 + kt[\mathrm{A}]_0$$

We see that the average chain length increases linearly with time.

Chain polymerizations proceed by adding monomers to the end of the growing polymer chain. As an example, we will look at radical polymerizations such as that of ethylene to form polyethylene:

$$\mathrm{R{-}CH_2CH_2\cdot} + \mathrm{CH_2CH_2} \rightarrow \mathrm{R{-}CH_2CH_2CH_2CH_2\cdot}$$

The reaction proceeds in three distinct reaction steps. During **initiation**, radicals are formed which subsequently start the chain reaction. In the example below, an initiator In is thermally decomposed to generate two radicals R ·. Other radical initiators are activated photochemically or through oxidation.



In general,

$$\mathrm{In} \xrightarrow{k_i} 2\,\mathrm{R}\cdot$$

$$\frac{d[\mathrm{R}\cdot]}{dt} = 2k_i[\mathrm{In}]$$

Subsequently, the radical reacts with a monomer M to give a radical $\mathrm{M}_1\cdot$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{\text{fast}} \mathrm{M}_1\cdot$$

During **propagation**, further monomers M are added, resulting in continuous chain growth:

$$\mathrm{M}_1\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_2\cdot$$

$$\mathrm{M}_2\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{M}_3\cdot$$

$$\vdots$$

To simplify matters we will assume that the monomer addition steps all proceed with the same rate constant k_p independent of chain length.

Chain **termination** occurs when two radical chains combine:

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \xrightarrow{k_t} \mathrm{M}_{n+m} \quad \text{(mutual termination)}$$

Here, we assume again that the rate is independent of the chain length. Other processes we will not consider in our simple treatment include the following:

$$\mathrm{M}_n\cdot + \mathrm{M}_m\cdot \rightarrow \mathrm{M}_n + \mathrm{M}_m \quad \text{(disproportionation)}$$

$$\mathrm{M}_n\cdot + \mathrm{M} \rightarrow \mathrm{M}_n + \mathrm{M}\cdot \quad \text{(chain transfer)}$$

In order to obtain a solution for the rate of polymer growth v_p,

$$v_p = -\frac{d[\mathrm{M}]}{dt} = k_p[\mathrm{M}\cdot][\mathrm{M}]$$

we apply the steady-state approximation to the concentration of all radical chains of any length $[\mathrm{M}\cdot]$, which we can assume to be small.

$$\frac{d[\mathrm{M}\cdot]}{dt} = 2fk_i[\mathrm{In}] - 2k_t[\mathrm{M}\cdot]^2 = 0$$

Here, we assume that the initiator radicals react instantaneously to form chain radicals with an efficiency f, which leads to the first term of the rate equation. The second term contains the rate of mutual termination. We find

$$[\mathrm{M}\cdot] = \left(\frac{fk_i}{k_t}\right)^{\frac{1}{2}} [\mathrm{In}]^{\frac{1}{2}}$$

so that

$$v_p = -\frac{d[\mathrm{M}]}{dt} = k_p \left(\frac{fk_i}{k_t}\right)^{\frac{1}{2}} [\mathrm{In}]^{\frac{1}{2}}[\mathrm{M}]$$

We can employ this expression to calculate the *kinetic chain length* λ

$$\lambda = \frac{\text{monomer units consumed}}{\text{activated centers produced}}$$

We can estimate this ratio by taking the ratio of the corresponding rates. Moreover, under steady-state conditions, the rate of activated center production will equal the rate of chain termination:

$$\lambda \approx \frac{\text{rate of monomer consumption}}{\text{rate of activated center production}} = \frac{k_p[\mathrm{M}\cdot][\mathrm{M}]}{2fk_i[\mathrm{In}]} \approx \frac{k_p[\mathrm{M}\cdot][\mathrm{M}]}{2k_t[\mathrm{M}\cdot]^2}$$

$$= \frac{k_p[\mathrm{M}]}{2k_t[\mathrm{M}\cdot]} = \frac{k_p}{2(fk_ik_t)^{\frac{1}{2}}}[\mathrm{In}]^{-\frac{1}{2}}[\mathrm{M}]$$

We obtain an estimate of the *degree of polymerization* $\langle N\rangle$ by assuming that all chains are terminated by mutual termination, so that

$$\langle N\rangle = 2\lambda = \frac{k_p}{(fk_ik_t)^{\frac{1}{2}}}[\mathrm{In}]^{-\frac{1}{2}}[\mathrm{M}]$$

We can see that a smaller initiator concentration will lead to a polymer with higher molecular weight.

4 THE KINETIC THEORY OF GASES

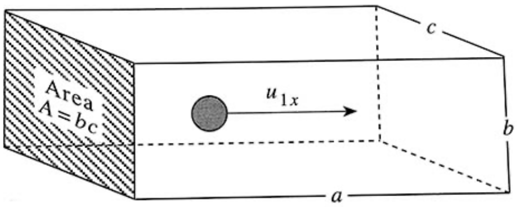
McQuarrie, D. A. & Simon, J. D. *Physical Chemistry: A Molecular Approach* Ch. 27. (University Science Books, 1997).

In the previous chapters of the course, we have covered various topics of macroscopic kinetics. We have studied a range of kinetic systems of varying complexity and have predicted their evolution based on the knowledge of the coupled rate equations that govern them as well as the rate constants involved. While we have discussed how to measure these rate constants, we have not addressed the question what determines the speed of a chemical reaction. If we want to predict rate constants from first principles, we need to develop a microscopic picture of chemical reactions, which we will do in the remainder of this course. We will begin with simple reactions in the gas phase that occur as gas molecules collide with each other. In contrast, the description of reactions in the condensed phase is vastly more complex due to the presence of solvent molecules that surround the reactants. Once we have developed a more detailed picture of gas-phase reactions, we can then transfer these concepts to more complicated reactions in solution.

Before we consider reactive collisions of gas molecules, we first introduce a simple model of gases, the **kinetic theory of gases**, which quantitatively describes the behavior of an ideal gas. At sufficiently low pressure, all gases, independently of their nature, behave as ideal gases. The kinetic gas theory describes such an ideal gas as an ensemble of molecules that are in constant motion. At low pressure, the average distance between two molecules is much larger than the molecular diameter, so that one can make the simplifying assumption that the gas molecules do not interact. Therefore, they do not possess any form of potential energy, but only kinetic energy, hence the name *kinetic theory of gases*. Collisions of two molecules are assumed to be collisions of hard spheres. They occur elastically, *i.e.* the total translational energy of molecules does not change during the collision; or in other words, no internal degrees of freedom (vibrations and rotations) are excited during the collision.

4.1 AVERAGE TRANSLATIONAL KINETIC ENERGY

Using these assumptions, we can calculate the pressure of an ideal gas and derive the ideal gas law. We consider a molecule of mass m with velocity components u_{1x}, u_{1y}, u_{1z} that moves in a container that for simplicity, we assume to be rectangular with sides a, b, c. Generalizing our approach to containers of arbitrary shape is straightforward.



When the molecule strikes the right wall, it exerts a force upon this wall that arises from the change of the x-component of its momentum mu_{1x}. If we assume that the collision is elastic, the momentum reverses sign, so that the absolute change in momentum becomes

$$\Delta(mu_{1x}) = |-mu_{1x} - mu_{1x}| = 2mu_{1x}$$

After the molecule bounces off the left wall, it will strike the right wall again after a roundtrip time of $\Delta t = 2\frac{a}{u_{1x}}$. The momentum per unit time imparted to the right wall therefore becomes

$$\frac{\Delta(mu_{1x})}{\Delta t} = \frac{mu_{1x}^2}{a} = F_1$$

According to Newton's second law this is equal to the force the molecule exerts on the right wall F_1. We obtain the associated pressure P_1 by dividing by the surface area of the right wall bc

$$P_1 = \frac{F_1}{bc} = \frac{mu_{1x}^2}{abc} = \frac{mu_{1x}^2}{V}$$

with $V = abc$ the volume of the container. We sum over all molecules to obtain the total pressure

$$P = \sum_{j=1}^{N} P_j = \sum_{j=1}^{N} \frac{mu_{jx}^2}{V} = \frac{m}{V}\sum_{j=1}^{N} u_{jx}^2$$

With $\sum_{j=1}^{N} u_{jx}^2 = N\langle u_x^2\rangle$, this leads to

$$PV = Nm\langle u_x^2\rangle$$

Because the gas is isotropic,

$$\langle u_x^2\rangle = \langle u_y^2\rangle = \langle u_z^2\rangle$$

And since $u^2 = u_x^2 + u_y^2 + u_z^2$, it follows that

$$\langle u^2\rangle = \langle u_x^2\rangle + \langle u_y^2\rangle + \langle u_z^2\rangle$$

so that

$$\langle u_x^2\rangle = \frac{1}{3}\langle u^2\rangle$$

and

$$PV = \frac{1}{3}Nm\langle u^2\rangle$$

From statistical thermodynamics, we know that the average translational energy per molecule of an ideal gas is

$$\langle\frac{1}{2}mu^2\rangle = \frac{1}{2}m\langle u^2\rangle = \frac{3}{2}k_BT$$

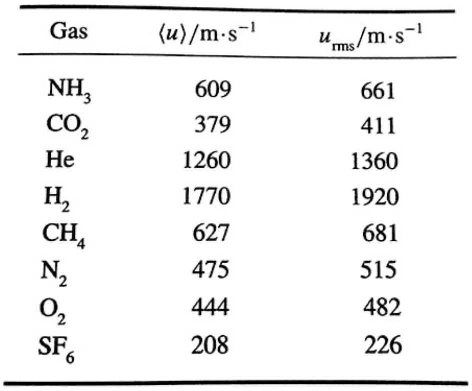
with the Boltzmann constant k_B. By substituting, we can thus derive the ideal gas law.

$$PV = Nk_BT = RnT$$

We can also derive an expression for the root-mean-square speed of a gas molecule

$$u_{rms} = \sqrt{\langle u^2\rangle} = \sqrt{\frac{3RT}{M}}$$

Note that because in general, $\langle u^2\rangle \neq \langle u\rangle^2$, the root-mean-square speed is generally different from the average speed, $u_{rms} \neq \langle u\rangle$. Nevertheless, at room temperature the difference is typically below 10%.



Gas	$\langle u\rangle/\mathrm{m\cdot s^{-1}}$	$u_{\mathrm{rms}}/\mathrm{m\cdot s^{-1}}$
NH_3	609	661
CO_2	379	411
He	1260	1360
H_2	1770	1920
CH_4	627	681
N_2	475	515
O_2	444	482
SF_6	208	226

Quiz: Use MATLAB to plot $u_{rms}(T)$ for H_2 and N_2.

4.2 THE MAXWELL-BOLTZMANN DISTRIBUTION

The speed distribution of a gas is described by the Maxwell-Boltzmann distribution, which we will derive here, following first the somewhat heuristic treatment of Maxwell, and then the more rigorous derivation of Boltzmann.

We are seeking an expression for the distribution function $h(u_x, u_y, u_z)$, which describes the probability $h(u_x, u_y, u_z)du_x du_y du_z$ that a molecule's velocity components fall between u_x and $u_x + du_x$; u_y and $u_y + du_y$; as well as u_z and $u_z + du_z$. We note that

$$\int_{-\infty}^{\infty} h(u_x, u_y, u_z)du_x du_y du_z = 1$$

Maxwell uses the assumption that the distributions of the different velocity components u_x, u_y, u_z are statistically independent of each other. This assumption, which turns out to be correct, allows us to write the speed distribution function as a product of the distributions of the individual components

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

The distributions for the x-, y-, and z-components must be identical because the gas is isotropic. For the same reason, the distribution should only depend on the speed, *i.e.* the magnitude of the velocity u, not its direction, where

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

We therefore introduce a new distribution function $\tilde{h}(u)$ that only depends on u and that we will use in the following. We take the logarithm of h and differentiate with respect to one velocity component

$$\ln h = \ln f(u_x) + \ln f(u_y) + \ln f(u_z)$$

$$\left(\frac{\partial \ln h}{\partial u_x}\right)_{u_y,u_z} = \frac{d \ln f(u_x)}{du_x}$$

We transform the partial derivate and introduce $\tilde{h}(u)$

$$\left(\frac{\partial \ln h}{\partial u_x}\right)_{u_y,u_z} = \frac{d \ln \tilde{h}}{du}\left(\frac{\partial u}{\partial u_x}\right)_{u_y,u_z} = \frac{u_x}{u}\frac{d \ln \tilde{h}}{du}$$

Quiz: Using $u^2 = u_x^2 + u_y^2 + u_z^2$, show that $\left(\frac{\partial u}{\partial u_x}\right)_{u_y,u_z} = \frac{u_x}{u}$.

Rearrangement gives

$$\frac{d\ln\tilde{h}}{udu} = \frac{d\ln f(u_x)}{u_x du_x} = \frac{d\ln f(u_y)}{u_y du_y} = \frac{d\ln f(u_z)}{u_z du_z}$$

Since u_x, u_y, and u_z are independent of each other, this expression must be equal to a constant, which we choose to be -2γ, so that

$$\frac{d\ln f(u_j)}{u_j du_j} = -2\gamma, j = x, y, z$$

and upon integration

$$f(u_j) = Ae^{-\gamma u_j^2}$$

Note that γ must be positive in order for the probability distribution $f(u_j)$ to be normalizable. Indeed, we can find A by setting

$$\int_{-\infty}^{\infty} f(u_j)du_j = A\int_{-\infty}^{\infty} e^{-\gamma u_j^2}du_j = 1$$

and obtain[1]

$$f(u_j) = \sqrt{\frac{\gamma}{\pi}}e^{-\gamma u_j^2}$$

We determine γ by calculating the average value of u_j^2, which we found in section 4.1 to be $\langle u_j^2\rangle = RT/M$, to that[2]

$$\langle u_j^2\rangle = \int_{-\infty}^{\infty} u_j^2 f(u_j)du_j = \sqrt{\frac{\gamma}{\pi}}\int_{-\infty}^{\infty} u_j^2 e^{-\gamma u_j^2}du_j = \frac{1}{2\gamma} = \frac{RT}{M}$$

which gives us the **probability distribution for a single velocity component**

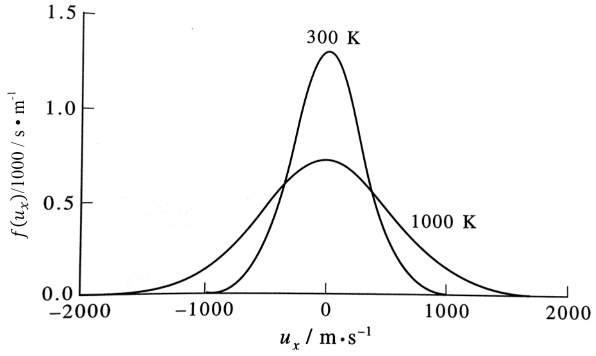
$$f(u_j) = \sqrt{\frac{M}{2\pi RT}}e^{-\frac{Mu_j^2}{2RT}} = \sqrt{\frac{m}{2\pi k_B T}}e^{-\frac{mu_j^2}{2k_B T}}$$

Quiz: Use MATLAB to plot $f(u_j)$ for H_2 and N_2 at different temperatures.

---

[1] $\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$

[2] $\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx = \frac{\sqrt{\pi}}{2a^{3/2}}$



One-dimensional velocity distribution of N_2 at 300 K and 1000 K.

Quiz: Determine the average value of the x-component of the velocity, $\langle u_j \rangle$, the average kinetic energy of the x-component of the velocity, $\langle E_{kin,x} \rangle$, as well as the average total kinetic energy, $\langle E_{kin,total} \rangle$.

Following **Boltzmann's approach**, we can arrive at the same result for the probability distribution for a single velocity component by using the Boltzmann distribution, a result of statistical thermodynamics. For a system at thermal equilibrium, the Boltzmann distribution describes the probability P_i of finding the system in a state of energy E_i

$$P_i = \frac{e^{-\frac{E_i}{k_B T}}}{\sum_j e^{-\frac{E_j}{k_B T}}} = \frac{e^{-\frac{E_i}{k_B T}}}{Q}$$

where $Q = \sum_j e^{-\frac{E_j}{k_B T}}$ is the partition function, and the sum is over all energy levels. The translational energy for one velocity component of a gas molecule is $\frac{1}{2} m u_j^2$, which leads to

$$f(u_j) = A e^{-\frac{\frac{1}{2} m u_j^2}{k_B T}}$$

which, after normalization, leads to the velocity distribution derived above.

In order to derive the speed distribution of an ideal gas $\tilde{h}(u)$ (*i.e.* the distribution of the magnitude of the velocity), we write down the three-dimensional velocity distribution function $h(u_x, u_y, u_z)$

$$\begin{aligned} h(u_x, u_y, u_z) du_x du_y du_z &= f(u_x) f(u_y) f(u_z) du_x du_y du_z \\ &= \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{m(u_x^2+u_y^2+u_z^2)}{2k_B T}} du_x du_y du_z \end{aligned}$$

and perform a coordinate transformation from Cartesian to polar coordinates with

$$u_x^2 + u_y^2 + u_z^2 = u^2$$

$$du_x du_y du_z = \left| \frac{\partial(u_x, u_y, u_z)}{\partial(u, \phi, \theta)} \right| du d\phi d\theta = u^2 \sin\theta \, du d\phi d\theta$$

so that we obtain

$$h'(u,\phi,\theta)dud\phi d\theta = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_BT}} dud\phi \sin\theta\, d\theta$$

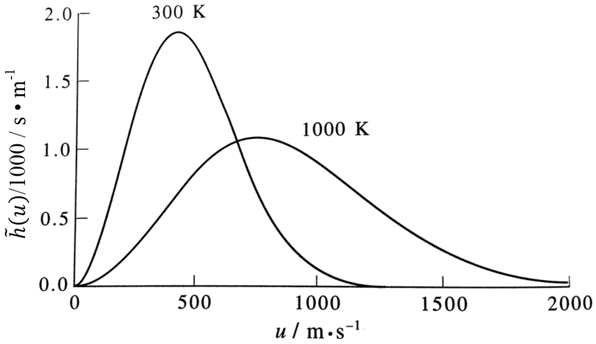
We eliminate the angular part through integration over φ and θ (we integrate over all directions in which the molecule can travel)

$$F(u)du = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_BT}} du \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_BT}} du$$

and thus obtain the Maxwell-Boltzmann distribution.

$$F(u)du = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} u^2 e^{-\frac{mu^2}{2k_BT}} du$$

Quiz: Use MATLAB to plot $F(u)$ for H_2 and N_2 at different temperatures. Compare with the escape velocity from earth.



Speed distribution of N_2 at 300 K and 1000 K.

Quiz: Derive the mean velocity $\langle u \rangle$ and the most probable velocity u^*.

Quiz: Derive the kinetic energy distribution $f(\varepsilon)d\varepsilon$, where ε is the kinetic energy of a molecule.

Quiz: Derive the mean energy $\langle \varepsilon \rangle$ and the most probable energy ε^*.

4.3 MEASUREMENTS OF THE VELOCITY DISTRIBUTION

As you have learnt in your spectroscopy course, the velocity distribution of the molecules in a gaseous sample leads to so-called Doppler broadening of the spectral transitions of the gas molecules. Measuring this broadening can therefore be used to infer the temperature of the gas. Due to the Doppler effect, a molecule moving towards the observer with a velocity u_x emits or absorbs radiation at a frequency ν that is shifted with respect the transition frequency ν_0 of the stationary molecule

$$\nu = \nu_0 \left(1 + \frac{u_x}{c}\right)$$

By substituting into the one-dimensional velocity distribution, we obtain the Doppler broadened line shape

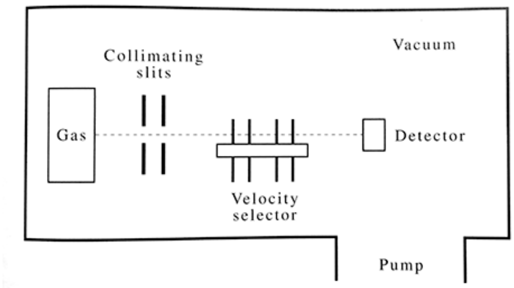
$$I(\nu) \propto e^{-\frac{mc^2(\nu-\nu_0)^2}{2\nu_0^2 k_B T}}$$

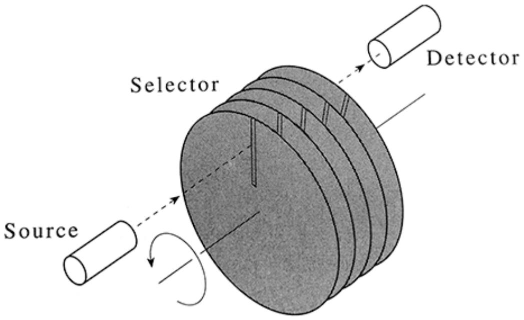
which is a gaussian with variance

$$\sigma^2 = \frac{v_0^2 k_B T}{mc^2}$$

which is proportional to the temperature.

The velocity distribution of a gas can also be measured with a setup as sketched below. In a vacuum chamber, a gas source emits a fine jet of gas molecules, which is collimated with apertures and passes through a velocity selector consisting of slits cut into series of spinning discs. The slit in each disc is displaced from that on the previous disc by a fixed angle, so that a given rotation speed will only allow molecules of one specific velocity to pass. A measurement of the gas flux exiting the discs as a function of the rotation frequency yields the velocity distribution.





5 COLLISIONS

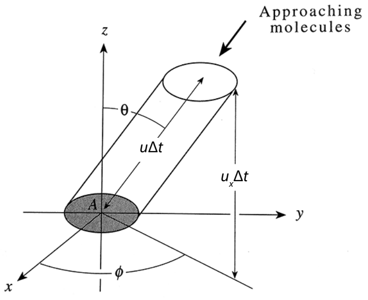
McQuarrie, D. A. & Simon, J. D. *Physical Chemistry: A Molecular Approach* Ch. 27. (University Science Books, 1997).

In order for a chemical reaction between to gaseous molecules to occur, they have to enter into spatial proximity – in other words they have to collide. Similarly, gas surface reactions require a collision between a gas molecule and the surface. In this chapter, we will therefore study collisions. We will build on the concepts from the kinetic theory of gases that we have developed in the previous chapter and look at different models of reactive collisions that differ in the complexity of how they treat the intermolecular interaction.

5.1 COLLISIONS WITH A WALL

In the following, we will derive the collision flux z_{coll} of gas molecules striking a surface, *i.e.* the number of molecules impinging on the surface per unit time and unit area. This is an important parameter for understanding gas-surface reactions that will also be useful in describing effusive beams. For a given gas density ρ, we use the Maxwell-Boltzmann distribution $F(u)$ to calculate the density of molecules $\rho_{u,\theta,\phi}$ moving at a given speed u and with polar angles θ and ϕ of the velocity vector.

$$\rho_{u,\theta,\phi} = \rho F(u) du \frac{\sin\theta \, d\theta d\phi}{4\pi}$$



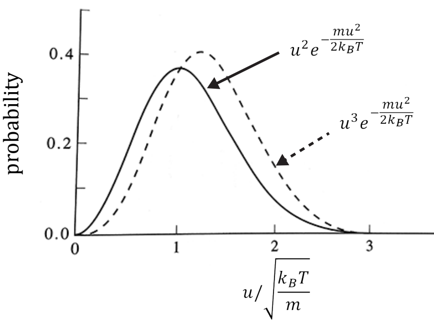
From the geometry sketched above, we can deduce that in a time interval Δt, all molecules with these parameters (u, θ, ϕ) will strike a circular area A if they are contained within the volume of an oblique cylinder of volume $V = Au_z\Delta t = Au\cos\theta\,\Delta t$. The number of molecules $N_{u,\theta,\phi}$ striking the area A during the time interval Δt is

$$N_{u,\theta,\phi} = V\rho_{u,\theta,\phi} = Au\cos\theta\,\Delta t\rho \cdot F(u)du\frac{\sin\theta\, d\theta d\phi}{4\pi}$$

We obtain the flux $z_{\mathrm{coll},u,\theta,\phi}$, *i.e.* the number of molecules with parameters (u, θ, ϕ) striking the surface per unit time and unit area by dividing by $A\Delta t$.

$$z_{\mathrm{coll},u,\theta,\phi} = \frac{N_{u,\theta,\phi}}{A\Delta t} = \frac{\rho}{4\pi} uF(u)du\cos\theta\sin\theta\, d\theta d\phi$$

Note that $z_{\mathrm{coll},u,\theta,\phi} \propto u^3$, since $uF(u) \propto u^3$. The distributions $F(u)$ and $uF(u)$ are plotted below, showing that the maximum of $uF(u)$ is shifted to higher values of u. This reflects the fact that faster molecules collide more frequently with the surface than slow ones.



Finally, we obtain the total flux z_{coll} by integrating over all molecular speeds u as well as all angles θ and ϕ.[3] Note that only molecules with $0 \le \theta \le \pi/2$ will hit the surface.

$$z_{\text{coll}} = \frac{\rho}{4\pi} \int_0^{\infty} uF(u)du \int_0^{\pi/2} \cos\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{\rho}{4}\langle u \rangle = \sqrt{\frac{k_BT}{2\pi m}}\rho$$

Quiz: Find a simplified derivation of the same result by using the one-dimensional velocity distribution.

Quiz: Calculate the collision flux of nitrogen at 300 K and 1 bar.

5.2 EFFUSION

Atkins, P. & de Paula, J. *Atkins' Physical Chemistry* Ch. 19A. (Oxford University Press, 2014).

Effusion occurs when gas escapes through a small hole into vacuum. According to Graham's law, the rate of effusion k_{effusion} is proportional to $\sqrt{1/M}$, where M is the molar mass of the gas. We can easily verify this empirical law from the above. For a hole with surface area A, we find

$$k_{\text{effusion}} = z_{\text{coll}}A = \sqrt{\frac{k_BT}{2\pi m}}\rho A \propto \sqrt{\frac{1}{m}}$$

This derivation assumes that the presence of the hole does not change the velocity distribution of the gas molecules, which is the condition for effusive flow to occur. This condition will be fulfilled if no collisions between gas molecules occur inside the hole, so that the velocity distribution of the molecules passing through the hole is not altered by the presence of the hole. This is the case, if the hole diameter is *small* compared to the mean free path of the gas molecules, *i.e.* the average distance between the collision of two gas molecules.

Through substitution with the ideal gas law, $\rho = p/(k_BT)$, we obtain

$$k_{\text{effusion}} = \sqrt{\frac{k_BT}{2\pi m}}\rho A = \frac{pA}{\sqrt{2\pi m k_BT}}$$

This equation is the basis for the *Knudsen method*, which is used to determine the vapor pressure of liquids and solids, particularly of low vapor pressure compounds. When a gas of known molecular mass effuses from a closed container through a small hole of known surface area, the mass loss is proportional to the vapor pressure of the compound.

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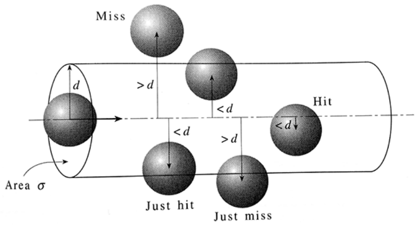
[3] $\int_0^{\pi/2} \cos\theta \sin\theta \, d\theta = \frac{1}{2}$

5.3 COLLISION RATE AND MEAN FREE PATH

Here we derive an expression for the frequency at which gaseous molecules collide. This collision rate, together with the probability that a collision leads to a chemical reaction, will then later allow us to calculate the speed of gas-phase chemical reactions.

We make the simplifying assumption that the molecules are hard spheres of diameter d, so that a collision occurs if the distance of two molecules is smaller than d, as illustrated below for a molecule moving from the left to the right.



We can see that this molecule will collide with every other molecule located within a cylinder of cross section $\sigma = \pi d^2$. We call this quantity σ the collision cross section. Within a time Δt, a molecule on average sweeps out a cylinder of volume $\sigma\langle u\rangle\Delta t$, where we have used the average speed $\langle u\rangle$ as derived above. Let us (wrongly) assume for the moment that all the other molecules are stationary. For a given gas density ρ, the molecule thus undergoes $\Delta N_{\text{coll}} = \rho\sigma\langle u\rangle\Delta t$ collisions. The collision rate z_A thus becomes

$$z_A = \frac{\Delta N_{\text{coll}}}{\Delta t} = \rho\sigma\langle u\rangle = \rho\sigma\sqrt{\frac{8k_BT}{\pi m}}$$

As the molecules within the collision cylinder are not stationary, however, we need to modify this result. Instead of the average speed of a single molecule $\langle u\rangle$, we should rather use the average relative speed of two molecules $\langle u_{AB}\rangle = \langle|\vec{u}_A - \vec{u}_B|\rangle$. By going to a center of mass coordinate system, we will derive this average speed difference to be

$$\langle u_{AB}\rangle = \langle|\vec{u}_A - \vec{u}_B|\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$$

where $\mu = \frac{m_1 m_2}{m_1+m_2}$ is the reduced mass. With $m_1 = m_2 = m$, we obtain $\mu = m/2$, so that

$$z_A = \rho\sigma\langle u_{AB}\rangle = \sqrt{2}\rho\sigma\langle u\rangle = \sqrt{2}\rho\sigma\sqrt{\frac{8k_BT}{\pi m}} = \rho\sigma\sqrt{\frac{8k_BT}{\pi\mu}}$$

Quiz: Calculate the collision rate of a single nitrogen molecule at 300 K and 1 bar, assuming $\sigma = 0.450 \cdot 10^{-18}\ \text{m}^2$.

A concept closely connected to the collision rate z_A is the **mean free path**, *i.e.* the average distance a molecule travels between collisions

$$l = \frac{\langle u\rangle}{z_A} = \frac{1}{\sqrt{2}\rho\sigma}$$

Quiz: Calculate the mean free path of nitrogen at 300 K and 1 bar, assuming $\sigma = 0.450 \cdot 10^{-18}\ \text{m}^2$.

We can also arrive at the same expression for the mean free path with a different approach. The number dN of collisions that a molecule will undergo in a collision cylinder of length dx is $dN = \sigma \rho dx$, so that the average number of collisions per unit length becomes $\frac{dN}{dx} = \sigma\rho$. A beam of n molecules crossing a gaseous sample thus gets attenuated (*i.e.* the number of unscattered molecules decreases) with a rate

$$\frac{dn}{dx} = -n\frac{dN}{dx} = -n\sigma\rho$$

which upon integration becomes

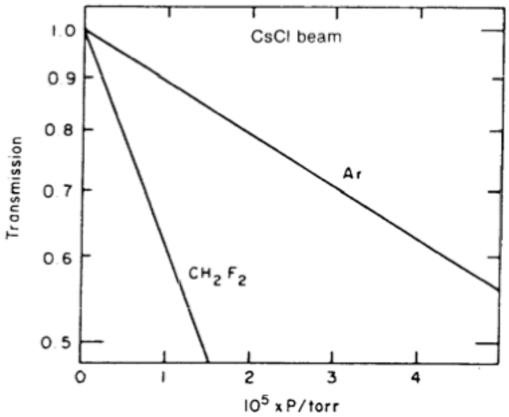
$$n = n_0 e^{-\sigma\rho x} = n_0 e^{-\frac{x}{l}}$$

where the mean free path l arises as the $\frac{1}{e}$ attenuation length. Note that in this derivation, the mean free path l is missing a factor of $1/\sqrt{2}$ because we have again incorrectly assumed that the molecules in the collision cylinder are stationary.
The probability $p(x)$ for a molecule to undergo a collision at x is

$$p(x) = -\frac{\frac{dn}{dx}}{n_0} = \frac{1}{l} e^{-\frac{x}{l}}$$

which we can use to verify that the mean free path $\langle x \rangle = \int_0^\infty x p(x) dx = l$.

By measuring the attenuation of a molecular beam crossing a gas cell as a function of pressure, one can determine the collision cross section.



Attenuation data for the scattering of a thermal beam of CsCl ($T \approx 1100$ K) by Ar atoms and by the polar molecule CH_2F_2 (both at 300 K) in a 44-mm cell. The logarithm of the transmission decreases linearly with target gas pressure P (and thus n_B). [Adapted from H. Schumacher, R. B. Bernstein, and E. W. Rothe, *J. Chem. Phys.*, *33*, 584 (1960).]

Another important quantity is the **total collision frequency**. In a pure gas, the total frequency of collisions per unit volume is

$$z_{AA} = \frac{1}{2}\rho z_A = \frac{1}{2}\rho^2 \sigma \sqrt{\frac{8k_B T}{\pi\mu}}$$

where the factor $\frac{1}{2}$ is introduced to avoid double counting collisions. In a mixture of gases, the total frequency of collisions per unit volume between the molecules of type A with those of type B is

$$z_{AB} = \sigma_{AB}\langle u_{AB}\rangle \rho_A \rho_B$$

with $\langle u_{AB}\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$, $\mu = \frac{m_1m_2}{m_1+m_2}$, and $\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2$.

5.4 CENTER OF MASS COORDINATES

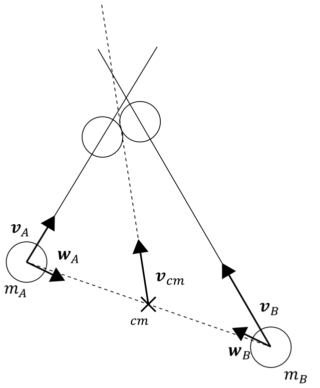
Bimolecular collisions are most easily described in center of mass coordinates, which we will derive here. To this end, we carry out the following coordinate transformation

$$(\boldsymbol{v}_A, \boldsymbol{v}_B) \rightarrow (\boldsymbol{v}_{cm}, \boldsymbol{w}_{AB})$$

where $(\boldsymbol{v}_A, \boldsymbol{v}_B)$ is the coordinate system given by the velocities of the molecules, and the new coordinate system $(\boldsymbol{v}_{cm}, \boldsymbol{w}_{AB})$ describes their motion in terms of the center of mass velocity $\boldsymbol{v}_{cm}$ as well as the relative velocity of both molecules $\boldsymbol{w}_{AB}$. This will then also allow us to determine the average relative speed of two molecules that we have used above for the calculation of the collision rate.

The center of mass cm of two molecules of masses m_A and m_B is the mass weighted average of their position vectors.

$$\boldsymbol{r}_{cm} = \frac{m_A\boldsymbol{r}_A + m_B\boldsymbol{r}_B}{m_A + m_B}$$



By taking the time derivative, we obtain

$$\frac{d\boldsymbol{r}_{cm}}{dt} = \boldsymbol{v}_{cm} = \frac{m_A\boldsymbol{v}_A + m_B\boldsymbol{v}_B}{m_A + m_B}$$

which shows that the center of mass is moving with a constant velocity $\boldsymbol{v}_{cm}$. By subtracting the velocity of the center of mass $\boldsymbol{v}_{cm}$ from the velocities of the molecules $\boldsymbol{v}_{A,B}$, we obtain the velocities $\boldsymbol{w}_{A,B}$ in the center of mass frame, *i.e.* in a moving coordinate system whose origin is the center of mass.

$$\boldsymbol{v}_A = \boldsymbol{v}_{cm} + \boldsymbol{w}_A$$
$$\boldsymbol{v}_B = \boldsymbol{v}_{cm} + \boldsymbol{w}_B$$

In these expressions, we wish to replace $\boldsymbol{w}_A$ and $\boldsymbol{w}_B$ with the relative velocity $\boldsymbol{w}_{AB}$ of the molecules in the center of mass frame

$$\boldsymbol{w}_{AB} = \boldsymbol{w}_A - \boldsymbol{w}_B = (\boldsymbol{w}_A + \boldsymbol{v}_{cm}) - (\boldsymbol{w}_B + \boldsymbol{v}_{cm}) = \boldsymbol{v}_A - \boldsymbol{v}_B = \boldsymbol{v}_{AB}$$

The sum of the momenta in the center of mass frame is zero.

$$m_A\boldsymbol{w}_A + m_B\boldsymbol{w}_B = m_A(\boldsymbol{v}_A - \boldsymbol{v}_{cm}) + m_B(\boldsymbol{v}_B - \boldsymbol{v}_{cm}) = m_A\boldsymbol{v}_A + m_B\boldsymbol{v}_B - (m_A + m_B)\boldsymbol{v}_{cm} = \boldsymbol{0}$$

This expression allows us to eliminate either $\boldsymbol{w}_A$ or $\boldsymbol{w}_B$ from the equation $\boldsymbol{w}_{AB} = \boldsymbol{w}_A - \boldsymbol{w}_B$, and we obtain

$$\boldsymbol{w}_{AB} = \boldsymbol{w}_A + \frac{m_A}{m_B}\boldsymbol{w}_A = m_A\boldsymbol{w}_A\frac{m_A + m_B}{m_A m_B}$$

We introduce the reduced mass

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

so that we can write

$$\mu\boldsymbol{w}_{AB} = m_A\boldsymbol{w}_A = -m_B\boldsymbol{w}_B$$

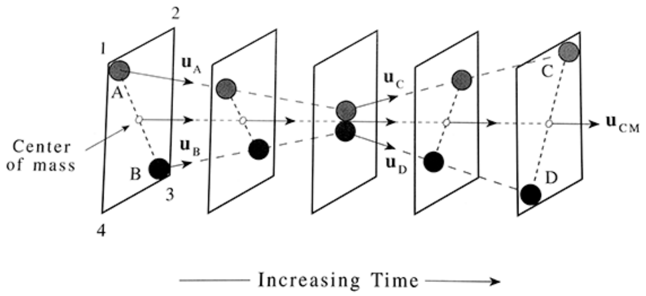
We thus find the following equations describing the coordinate transformation:

$$\begin{aligned}\boldsymbol{v}_A &= \boldsymbol{v}_{cm} + \mu\boldsymbol{w}_{AB}/m_A\\ \boldsymbol{v}_B &= \boldsymbol{v}_{cm} - \mu\boldsymbol{w}_{AB}/m_B\end{aligned}$$

The total kinetic energy of the system is given by

$$\begin{aligned}E_{\text{kin}} &= \frac{1}{2}m_A\boldsymbol{v}_A^2 + \frac{1}{2}m_B\boldsymbol{v}_B^2 = \frac{1}{2}m_A\left(\boldsymbol{v}_{cm} + \frac{\mu\boldsymbol{w}_{AB}}{m_A}\right)^2 + \frac{1}{2}m_B\left(\boldsymbol{v}_{cm} - \frac{\mu\boldsymbol{w}_{AB}}{m_B}\right)^2\\ &= \frac{1}{2}(m_A + m_B)v_{cm}^2 + \frac{1}{2}\mu w_{AB}^2 + \boldsymbol{v}_{cm}\mu\boldsymbol{w}_{AB} - \boldsymbol{v}_{cm}\mu\boldsymbol{w}_{AB}\\ &= \frac{1}{2}(m_A + m_B)v_{cm}^2 + \frac{1}{2}\mu v_{AB}^2 = E_{\text{kin, cm}} + E_{\text{kin, AB}}\end{aligned}$$

We can thus see that the total kinetic energy is composed of the kinetic energy involved in the motion of the center of mass, which is associated with the mass $m_A + m_B$; and that of relative motion of the molecules in the center of mass frame, which is associated with the reduced mass μ.
As the two contributions to the kinetic energy suggest, we can view the collision as the relative motion of the molecules superimposed on the center of mass motion.



After the collision, we obtain for the center of mass velocity of the product molecules C and D (whose masses may differ from those of the reactants)

$$\boldsymbol{v}_{cm} = \frac{m_C\boldsymbol{v}_C + m_D\boldsymbol{v}_D}{m_C + m_D}$$

Since the total momentum must be conserved

$$m_C\boldsymbol{v}_C + m_D\boldsymbol{v}_D = m_A\boldsymbol{v}_A + m_B\boldsymbol{v}_B$$

we find that the center of mass velocity does not change during the collision. Therefore, the kinetic energy of the center of mass motion $E_{\text{kin, cm}} = \frac{1}{2}(m_A + m_B)\boldsymbol{v}_{cm}^2$ remains unchanged, so that we can neglect it if we want to describe a chemical reaction. Only the kinetic energy associated with the relative motion $E_{\text{kin, AB}} = \frac{1}{2}\mu\boldsymbol{v}_{AB}^2$ is available for the reaction. While the relative velocity may change during the course of a collision, the sum of the relative kinetic energy and internal energy must remain constant.

$$E_{\text{internal, A,B}} + E_{\text{kin, AB}} = E_{\text{internal, C,D}} + E_{\text{kin, CD}}$$

The expression for the kinetic energy will be useful in deriving the average relative speed of both molecules. We begin by writing down the velocity distribution of the two molecules, which is simply the product of two Maxwell-Boltzmann distributions.

$$\begin{aligned} &f(v_{Ax}, v_{Ay}, v_{Az}, v_{Bx}, v_{By}, v_{Bz})dv_{Ax}dv_{Ay}dv_{Az}dv_{Bx}dv_{By}dv_{Bz} \\ &= \frac{(m_Am_B)^{\frac{3}{2}}}{(2\pi k_BT)^3} e^{-\frac{m_Av_A^2+m_Bv_B^2}{2k_BT}} dv_{Ax}dv_{Ay}dv_{Az}dv_{Bx}dv_{By}dv_{Bz} \end{aligned}$$

After carrying out the coordinate transformation, we obtain[4]

$$\begin{aligned} &f(v_{cm,x}, v_{cm,y}, v_{cm,z}, v_{ABx}, v_{ABy}, v_{ABz})dv_{cm,x}dv_{cm,y}dv_{cm,z}dv_{AB,x}dv_{AB,y}dv_{AB,z} \\ &= \frac{(m_Am_B)^{\frac{3}{2}}}{(2\pi k_BT)^3} e^{-\frac{(m_A+m_B)v_{cm}^2+\mu v_{AB}^2}{2k_BT}} dv_{cm,x}dv_{cm,y}dv_{cm,z}dv_{AB,x}dv_{AB,y}dv_{AB,z} \\ &= (m_Am_B)^{\frac{3}{2}}\left[\frac{1}{(2\pi k_BT)^{\frac{3}{2}}} e^{-\frac{(m_A+m_B)v_{cm}^2}{2k_BT}} dv_{cm,x}dv_{cm,y}dv_{cm,z}\right]\left[\frac{1}{(2\pi k_BT)^{\frac{3}{2}}} e^{-\frac{\mu v_{AB}^2}{2k_BT}} dv_{AB,x}dv_{AB,y}dv_{AB,z}\right] \end{aligned}$$

We eliminate the terms containing the center of mass part by integrating over all center of mass velocities, with

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{1}{(2\pi k_BT)^{\frac{3}{2}}} e^{-\frac{(m_A+m_B)v_{cm}^2}{2k_BT}} dv_{cm,x}dv_{cm,y}dv_{cm,z} = \frac{1}{(m_A + m_B)^{\frac{3}{2}}}$$

We are left with

$$f(v_{ABx}, v_{ABy}, v_{ABz})dv_{AB,x}dv_{AB,y}dv_{AB,z} = \left(\frac{\mu}{2\pi k_BT}\right)^{\frac{3}{2}} e^{-\frac{\mu v_{AB}^2}{2k_BT}} dv_{AB,x}dv_{AB,y}dv_{AB,z}$$

As in the derivation of the Maxwell-Boltzmann distribution, we transform to spherical coordinates[5]

$$f(v_{\text{AB}}, \phi, \theta)dv_{\text{AB}}d\phi d\theta = \left(\frac{\mu}{2\pi k_BT}\right)^{\frac{3}{2}} v_{\text{AB}}^2 e^{-\frac{\mu v_{AB}^2}{2k_BT}} \sin\theta \, dv_{\text{AB}}d\phi d\theta$$

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[4] $dv_{Ax}dv_{Ay}dv_{Az}dv_{Bx}dv_{By}dv_{Bz} = dv_{cm,x}dv_{cm,y}dv_{cm,z}dv_{AB,x}dv_{AB,y}dv_{AB,z}$ (Derive!)

[5] $dv_{AB,x}dv_{AB,y}dv_{AB,z} = v_{\text{AB}}^2 \sin\theta \, dv_{\text{AB}}d\phi d\theta$

and integrate over all angles[6] to obtain

$$f(v_{\mathrm{AB}})dv_{\mathrm{AB}} = 4\pi\left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v_{\mathrm{AB}}^2 e^{-\frac{\mu v_{AB}^2}{2k_B T}} dv_{\mathrm{AB}}$$

This is the distribution of the relative speed v_{AB} of two molecules, which is a Maxwell-Boltzmann distribution containing the reduced mass μ instead of the molecular mass.

For $m_1 = m_2 = m$, we find that $\mu = m/2$. Therefore $\langle v_{\mathrm{AB}}\rangle = \sqrt{2}\langle v_{\mathrm{A}}\rangle$, which we have used above.

5.5 DYNAMICS OF BIMOLECULAR COLLISIONS – REACTIVE HARD SPHERES

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 8. (Prentice Hall, 1989).

In this section, we will study the dynamics of bimolecular collisions. Based on the results from the kinetic theory of gases, we can derive simple expressions for the rate constants of bimolecular gas-phase reactions. Initially, we will assume that the reacting molecules are hard spheres. We will then obtain a more accurate picture by considering more complex intermolecular potentials. Finally, we will discuss solving Hamilton's equations of motions on the potential energy surface and solving Schrödinger's equation to obtain a quantum mechanical solution.

Above, we have derived the collision rate per unit volume of two molecules

$$z_{AB} = \sigma_{AB}\langle u_{AB}\rangle \rho_A \rho_B$$

with $\langle u_{AB}\rangle = \sqrt{\frac{8k_BT}{\pi\mu}}$, $\mu = \frac{m_1 m_2}{m_1+m_2}$, and $\sigma_{AB} = \pi\left(\frac{d_A+d_B}{2}\right)^2$. Assuming every collision leads to a reaction, we obtain a rate constant for the bimolecular reaction

$$k(T) = \sigma_{AB}\langle u_{AB}\rangle = \pi\left(\frac{d_A+d_B}{2}\right)^2 \cdot \sqrt{\frac{8k_BT}{\pi\mu}}$$

This rate grossly overestimates experimentally determined reaction rates, since for most gas-phase reactions, not every collision leads to a chemical reaction. Moreover, the model predicts that $k(T) \propto \sqrt{T}$, whereas experimentally, one typically finds Arrhenius behavior with $k(T) \propto e^{-E_{\mathrm{act}}/k_BT}$.
The reactive hard spheres model addresses some of these issues by taking a refined view of the molecular interaction. The sketch below depicts a collision between two molecules A and B, which we assume to be hard spheres. The molecules collide at a relative velocity $\boldsymbol{v}_{AB} = \boldsymbol{v}$, *i.e.* with an energy $E = \frac{1}{2}\mu v^2$. The minimum distance is $d = \frac{1}{2}(d_A + d_B)$. To describe the collision geometry, we furthermore introduce the **impact parameter** b, which describes the center distance of the spheres in the direction orthogonal to the velocity vector $\boldsymbol{v}$.

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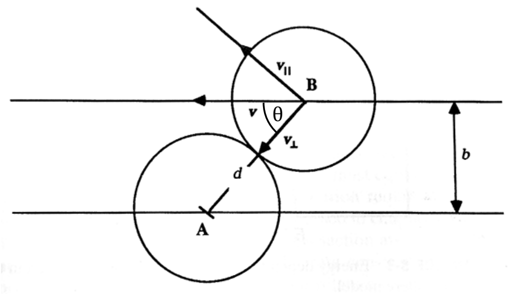
[6] $\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta = 4\pi$



The velocity vector $\boldsymbol{v}$ can be decomposed into a tangential component $\boldsymbol{v}_{\parallel}$ (parallel to the tangent plane of the two spheres) and a component $\boldsymbol{v}_{\perp}$ that is orthogonal to it. We can similarly decompose the kinetic energy

$$E = \frac{1}{2}\mu v_{\parallel}^2 + \frac{1}{2}\mu v_{\perp}^2 = E_{\parallel} + E_{\perp}$$

where only the second term $E_{\perp} = \frac{1}{2}\mu v_{\perp}^2$ is assumed to be available to drive the reaction as it arises from motion along the line of centers. With the angle θ between the velocity vectors $\boldsymbol{v}$ and $\boldsymbol{v}_{\perp}$, we find that

$$\frac{E_{\perp}}{E} = \frac{v_{\perp}^2}{v^2} = \cos^2\theta = 1 - \sin^2\theta = 1 - \frac{b^2}{d^2}$$

Furthermore, the model assumes that the reaction will only occur above a certain minimum collision energy E^* along the line of centers. The energy dependent reaction probability $P_R(E_{\perp})$ is therefore defined to be

$$P_R(E_{\perp}) = \begin{cases} 0 & \text{if } E_{\perp} < E^* \\ p & \text{if } E_{\perp} \geq E^* \end{cases}$$

where above threshold, the reaction occurs with a probability p. This leads to a reaction cross section that depends both on the energy E as well as the impact parameter b. Since we usually cannot control the impact parameter, we integrate to obtain the reaction cross section $\sigma_R(E)$ that only depends on the energy

$$\sigma_R(E) = \int_0^{\infty} P_R(E_{\perp}) \cdot 2\pi b \, db$$

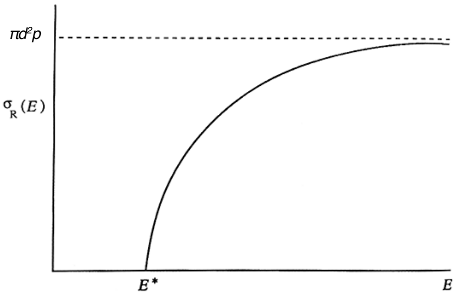
We can see that for $E < E^*$, $\sigma_R(E) = 0$.

For $E \geq E^*$, we have to calculate the integral. From $E_{\perp} = E(1 - \frac{b^2}{d^2}) \geq E^*$, we obtain $b \leq d\sqrt{1 - \frac{E^*}{E}}$, so that we can change the integral boundaries.

$$\sigma_R(E) = \int_0^{d\sqrt{1-\frac{E^*}{E}}} p \cdot 2\pi b db = \pi d^2 p (1 - \frac{E^*}{E})$$

We thus obtain

$$\sigma_R(E) = \begin{cases} 0 & \text{if } E < E^* \\ \pi d^2 p (1 - \frac{E^*}{E}) & \text{if } E \geq E^* \end{cases}$$



To obtain the thermal rate coefficient $k(T) = \langle \sigma_R(E) v(E) \rangle$, we average over a thermal population of molecules as given by the Maxwell-Boltzmann distribution $F(v)$ for the relative speed

$$k(T) = \int_0^\infty \sigma_R(E) v \cdot F(v) dv = \int_0^\infty \sigma_R(E) v \cdot 4\pi \left(\frac{\mu}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{\mu v^2}{2k_B T}} dv$$

We transform the integral[7] and change the boundaries to reflect that the cross section is zero for $E < E^*$

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{\frac{1}{2}} \int_0^\infty E\sigma_R(E) e^{-\frac{E}{k_B T}} dE = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{\frac{1}{2}} \int_{E^*}^\infty \pi d^2 p(E - E^*) e^{-\frac{E}{k_B T}} dE$$

After integration, we obtain[8]

$$k(T) = \pi d^2 \left(\frac{8 k_B T}{\pi\mu}\right)^{\frac{1}{2}} p e^{-\frac{E^*}{k_B T}}$$

Note that the rate constant is a product of three factors.

hard-sphere cross section × mean velocity × Arrhenius factor

If we compare with the Arrhenius law, $k_{\text{Arrhenius}} = Ae^{-\frac{E_a}{k_B T}}$, with $\frac{d(\ln k_{\text{Arrhenius}})}{d(1/T)} = -\frac{E_a}{k_B}$, we find a similar temperature dependence

$$\frac{d(\ln k)}{d(1/T)} = -\frac{T}{2} - \frac{E^*}{k_B}$$

and see that the threshold energy E^* corresponds to the Arrhenius activation energy E_a, while the product of hard-sphere cross section and mean velocity corresponds to the prefactor. With a reaction probability of $p = 1$, the model tends to overestimate the rate constant. Therefore, $p < 1$ is introduced as an *ad hoc* correction to account for collisions that possess sufficient energy, but still are not reactive. The variable p is called the **steric factor**, encapsulating the notion that not all molecular orientations in a collision will lead to a reaction. We can already guess that ultimately, this steric factor is related to the entropy of activation.

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[7] $E = \frac{1}{2}\mu v^2, dv = \frac{dE}{\mu v}$

[8] $\int_0^\infty x e^{-\frac{x}{a}} dx = a^2$

5.6 AN APPLICATION TO TOLMAN'S THEOREM

Laidler, K. J. *Chemical Kinetics*, Section 3.1.2. (Prentice Hall, 1987).

The thermal rate constant for bimolecular reactions derived above allows us to demonstrate Tolman's theorem, which provides insights into the nature of the activation energy of a chemical reaction. It states that the activation energy of a molecule E_a is equal to the difference between the mean energy of the reacting molecules $\langle E_R \rangle$ and the mean energy of all molecules $\langle E \rangle$.

$$E_a = \langle E_R \rangle - \langle E \rangle$$

We will show that this holds for a bimolecular gas-phase reaction with an energy dependent reaction cross section $\sigma_R(E)$. For the thermal rate constant $k(T)$, we found above

$$k(T) = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{\frac{1}{2}} \int_0^\infty E\sigma_R(E)e^{-\frac{E}{k_B T}}dE = \frac{1}{k_B T}\left(\frac{8}{\pi\mu k_B T}\right)^{\frac{1}{2}} \int_0^\infty g(E)dE$$

where we have introduced the function $g(E)$, which is proportional to the reaction rate $k(E)$ at one specific energy.

$$E_a = k_B T^2 \frac{d\ln k(T)}{dT} = -\frac{3}{2}k_B T + k_B T^2 \frac{d\ln \int_0^\infty g(E)dE}{dT}$$

We can simplify

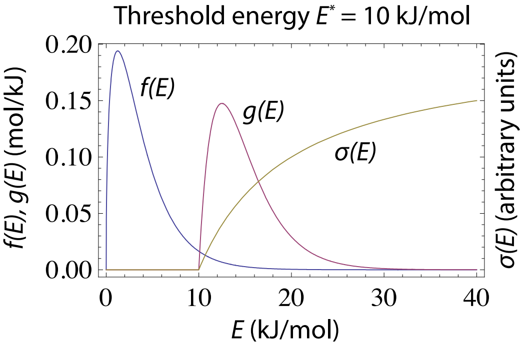
$$\frac{d\ln \int_0^\infty g(E)dE}{dT} = \frac{\frac{d}{dT}\int_0^\infty g(E)dE}{\int_0^\infty g(E)dE} = \frac{\int_0^\infty \frac{E}{k_B T^2} g(E)dE}{\int_0^\infty g(E)dE}$$

so that we find

$$E_a = \frac{\int_0^\infty Eg(E)dE}{\int_0^\infty g(E)dE} - \frac{3}{2}k_B T = \langle E_R \rangle - \langle E \rangle$$

which is indeed Tolman's theorem.

The energy distribution of all molecules $f(E)$ as well as that of the reactive molecules $g(E)$ is shown below together with the collision cross section $\sigma(E)$ for the reactive hard sphere model. It is apparent that the mean energies differ by the chosen threshold energy $E^* = 10$ kJ/mol.



If we calculate the activation energy E_a for the reactive hard sphere model (with $p = 1$), we find indeed

$$E_a = \frac{\int_0^\infty E g(E) dE}{\int_0^\infty g(E) dE} - \frac{3}{2} k_B T = \frac{\int_{E^*}^\infty E^2 \pi d^2 \left(1 - \frac{E^*}{E}\right) e^{-\frac{E}{k_B T}} dE}{\int_{E^*}^\infty E \pi d^2 \left(1 - \frac{E^*}{E}\right) e^{-\frac{E}{k_B T}} dE} - \frac{3}{2} k_B T$$

$$= \frac{\int_{E^*}^\infty (E^2 - E E^*) e^{-\frac{E}{k_B T}} dE}{\int_{E^*}^\infty (E - E^*) e^{-\frac{E}{k_B T}} dE} - \frac{3}{2} k_B T = E^* - \frac{3}{2} k_B T$$

5.7 DYNAMICS OF BIMOLECULAR COLLISIONS – TWO-BODY CLASSICAL SCATTERING

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 8. (Prentice Hall, 1989).

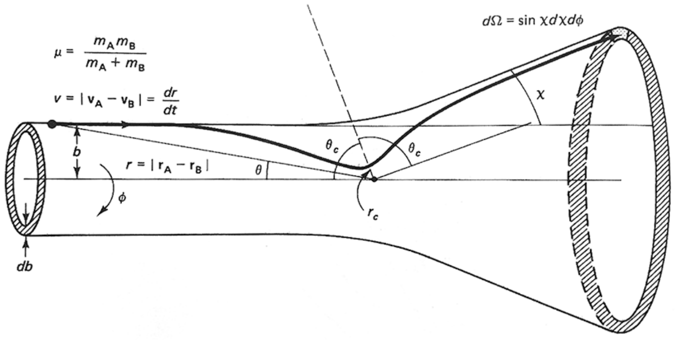
In this section, we will develop a classical description of bimolecular collisions in order to derive differential and total scattering cross sections. We assume that the particles interact through a central potential $U(r)$, where r is the distance between the particles. Strictly speaking, such a description is still only valid for simple systems, such as the collision of two rare gas atoms, whereas many chemical reactions of interest will involve more than two atoms. However, analytical solutions only exist for the two-body problem. Most importantly, the description of two-body scattering with a central potential will allow us to develop general concepts that will be useful even for more complex bimolecular reactions.

We begin by considering the total energy of the two colliding particles A and B, which consists of kinetic, potential, and internal energy.

$$E = \frac{1}{2} m v_A^2 + \frac{1}{2} m v_B^2 + U(r) + E_{A,\,\text{internal}} + E_{B,\,\text{internal}}$$

We can distinguish different types of collisions. In an **elastic collision**, the internal energies of the particles are left unchanged, whereas in an **inelastic collision**, translational energy is converted into internal energy or vice versa. Finally, in a **reactive collision**, the molecular species also change their nature.

Due to the symmetry of the central potential $U(r)$ through which the particles interact, it is convenient to describe the collision in a **fixed-center-of-force** coordinate system. As before, we transform into a center of mass coordinate system, in which a composite particle AB of reduced mass $\mu = m_A m_B/(m_A + m_B)$ appears to move along the trajectory $\boldsymbol{r}(t) = \boldsymbol{r}_A(t) - \boldsymbol{r}_B(t)$. We describe this motion in polar coordinates (r, θ, ϕ) with the origin of the coordinate system coinciding with the center of the potential $U(r)$. The scattering geometry in the fixed-center-of-force coordinate system together with the pertinent variables is sketched below.



The composite particle AB has coordinates (r,θ,ϕ) and travels at velocity $\frac{dr}{dt}$. The particle is thought to originate at infinite distance, travelling parallel to the x axis with an impact parameter b. The interaction with the central potential leads to a deflection of the trajectory by an angle $\chi(b)$ that is a function of the impact parameter. Note that for a spherical potential $U(r)$, the scattering process is confined to a plane, so that the azimuthal angle ϕ does not change during the collision and the entire scattering geometry has cylindrical symmetry. We will therefore find that there is no dependence on the azimuthal angle ϕ.

Particles originating in the differential surface element $d(\pi b^2)$ are scattered into a solid angle $d\Omega = \sin\chi\, d\chi d\phi$. Overall, the total particle flux must be conserved, which we can express as follows

$$\sigma_R(v,\Gamma) = \int P_R(v,b;\Gamma)\, 2\pi b db = \iint I_R(\chi,\phi;v,\Gamma) d\Omega$$

Here, $\sigma_R(v,\Gamma)$ is the total scattering cross section, with v and Γ the particle velocity and internal state, respectively. As we have seen before, the total scattering cross section can be obtained by multiplying each surface element $d(\pi b^2) = 2\pi b db$ with its corresponding reaction probability $P_R(v,b;\Gamma)$ and integrating over all impact parameters. The integral $\int P_R(v,b;\Gamma)\, 2\pi b db$ therefore corresponds to the incoming beam. We can also obtain the total scattering cross section by integrating the differential cross section $I_R(\chi,\phi;v,\Gamma)$ over the entire solid angle, $\iint I_R(\chi,\phi;v,\Gamma) d\Omega$. This integral corresponds to the scattered beam.

To derive the partial scattering cross section of the elastic collisions of particles interacting through a central potential, we first try to find the deflection function $\chi(b)$. We begin by writing down the total energy of the particle. In Cartesian coordinates, the energy of a particle moving in the xz-plane is

$$E = \frac{1}{2}\mu\dot{x}^2 + \frac{1}{2}\mu\dot{z}^2 + U(r)$$

We transform into polar coordinates and obtain (prove!)

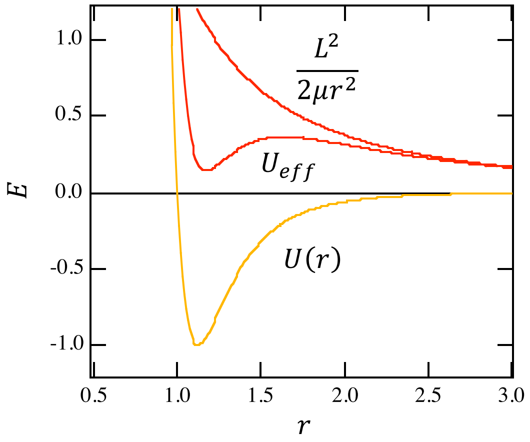
$$E = \frac{1}{2}\mu(\overset{\cdot}{r\cos\theta})^2 + \frac{1}{2}\mu(\overset{\cdot}{r\sin\theta})^2 + U(r) = \frac{1}{2}\mu\dot{r}^2 + \frac{1}{2}\mu r^2\dot{\theta}^2 + U(r) = \cdots$$

$$E = \frac{1}{2}\mu v^2 + \frac{L^2}{2\mu r^2} + U(r)$$

where $L = \mu v_0 b = \mu v' b'$ is the angular momentum, with v_0 the initial velocity and the primes denoting the variables after the collision.

A particle of non-zero angular momentum $L \neq 0$ experiences a repulsive force in its radial motion due to the rotational energy term $\frac{L^2}{2\mu r^2}$ that is termed **centrifugal barrier**. The particle experiences an effective potential

$$U_{eff} = \frac{L^2}{2\mu r^2} + U(r)$$



We derive the trajectory $\theta(r)$ from the equations for the conserved quantities, the angular moment L and the energy E.

$$L = \mu r^2 \frac{d\theta}{dt}; \quad d\theta = \frac{L}{\mu r^2} dt$$

$$E = \frac{1}{2}\mu\left(\frac{dr}{dt}\right)^2 + \frac{L^2}{2\mu r^2} + U(r); \quad dt = -\left[\frac{2}{\mu}\left(E - U(r) - \frac{L^2}{2\mu r^2}\right)\right]^{-\frac{1}{2}} dr$$

We substitute dt to obtain

$$d\theta = -\frac{L}{\mu r^2}\left[\frac{2}{\mu}\left(E - U(r) - \frac{L^2}{2\mu r^2}\right)\right]^{-\frac{1}{2}} dr$$

Before integrating this equation, we substitute $L = \mu v_0 b = b(2\mu E)^{\frac{1}{2}}$, where we have used $v_0 = \sqrt{\frac{2E}{\mu}}$. This can be seen by realizing that initially, the particle is at infinite distance ($r \to \infty$), so that its potential energy is zero for any well-behaved potential energy function, $U(r \to \infty) = 0$. Moreover, the rotational energy must be zero, $\frac{L^2}{2\mu(r\to\infty)^2} = 0$, so that the particle only has kinetic energy, *i.e.*

$$E = \frac{1}{2}\mu v_0^2$$

Substitution of L gives

$$d\theta = -b \frac{dr}{r^2\left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$

Finally, we obtain $\theta(r)$ through integration

$$\theta(r) = -b \int_{\infty}^{r} \frac{dr}{r^2\left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$

The sketch of the scattering geometry shows that every trajectory has a point (r_c, θ_c) at which the particle has a minimum distance r_c from the origin and at which $\frac{dr}{dt} = 0$. In other words, the particle moves only tangentially, and its energy is composed of potential and rotational energy only. Note that because of the symmetry of the potential, the trajectory is symmetric with respect to a line through (r_c, θ_c) and the origin. Therefore, we find for the total deflection angle $\chi = \pi - 2\,\theta_c$, as can be seen in the sketch above.

$$\chi(E,b) = \pi - 2\,\theta_c = \pi - 2b \int_{r_c}^{\infty} \frac{dr}{r^2 \left[1 - \frac{U(r)}{E} - \frac{b^2}{r^2}\right]^{\frac{1}{2}}}$$

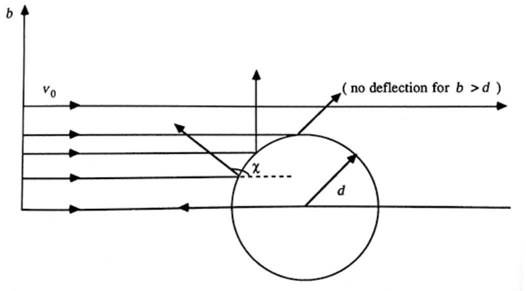
We can now obtain deflection functions for different central potentials. We will again start with the **hard-sphere potential** with

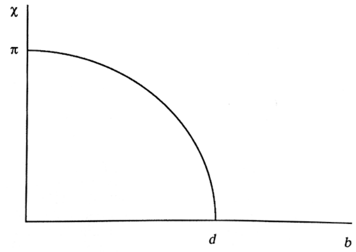
$$U(r) = \begin{cases} 0 & (r > d) \\ \infty & (r \leq d) \end{cases}$$

and $r_c = d$ for collisions at any energy. We find

$$\chi(E,b) = \pi - 2b \int_{d}^{\infty} \frac{dr}{r^2 \left[1 - \frac{b^2}{r^2}\right]^{\frac{1}{2}}} = \cdots = 2\arccos\frac{b}{d}$$

We note that for $b > d$, the acos function is not defined, and no collision occurs, so that $\chi(E, b > d) = 0$. Moreover, we find that the deflection function is energy independent. Trajectories of hard-sphere collisions and the corresponding deflection function are shown below.





From the deflection function, we can calculate the differential cross section. For hard-sphere collisions, $\chi(b)$ is a monotonic function that maps one specific deflection angle χ to one specific impact parameter b. In this case, molecules from the annular element $2\pi b db$ are deflected into the solid angle element $\sin\chi\, d\chi \int_0^{2\pi} d\phi = 2\pi \sin\chi\, d\chi$, and we can write

$$I(E,\chi)|2\pi \sin\chi\, d\chi| = 2\pi b db$$

$$I(E,\chi) = \frac{b}{\left|\sin\chi \frac{d\chi}{db}\right|} = \frac{b}{\left|\frac{d(\cos\chi)}{db}\right|} = \cdots = \frac{d^2}{4}$$

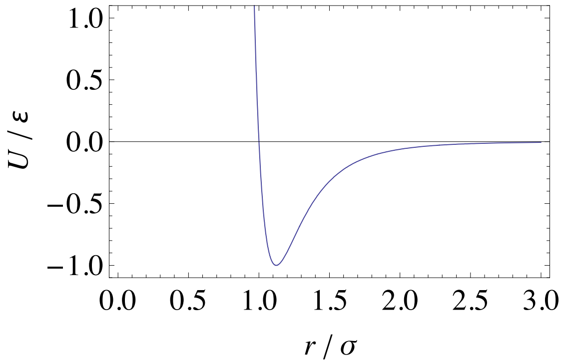
The differential scattering cross section is thus independent of the energy E as well as the angle (in the center of mass system). We can integrate the differential cross section $I(E,\chi)$ in order to obtain the total cross section

$$\sigma(E) = 4\pi \frac{d^2}{4} = \pi d^2$$

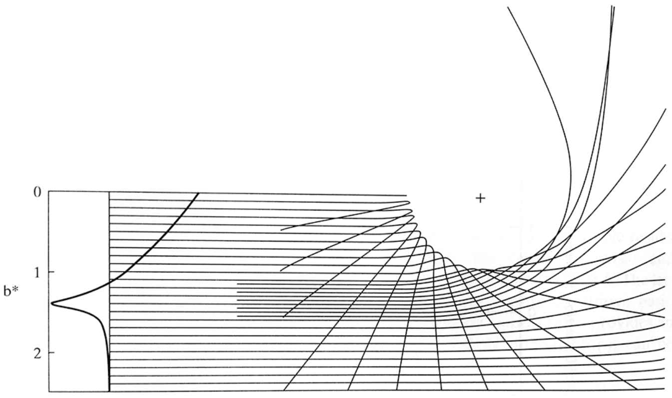
which is the hard-sphere collision cross section we derived before.

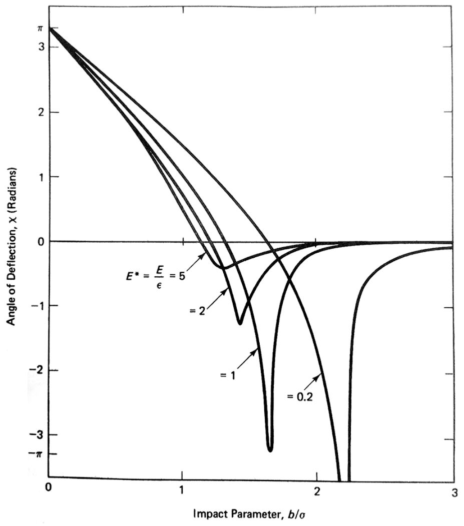
The **Lennard-Jones potential** is a frequently used model potential that describes the intermolecular interaction more realistically.

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



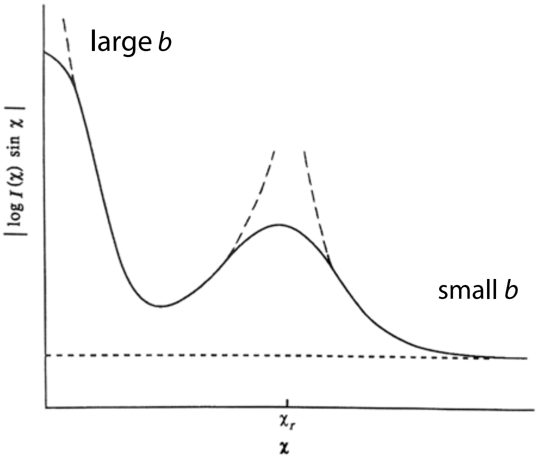
Here, ϵ characterizes the depth of the potential well. The $\left(\frac{\sigma}{r}\right)^{6}$ term describes a long-range attraction, while the $\left(\frac{\sigma}{r}\right)^{12}$ term describes the intermolecular repulsion that sets in at short distances. Trajectories for the Lennard-Jones potential as well as the deflection function are shown below.





A comparison with the hard-sphere deflection function provides some insights.
For *small impact parameter* ($b \to 0$), the deflection function resembles the hard-sphere one. For these head-on collisions, the particle largely interacts with the steep repulsive part of the potential, which it encounters at its closest approach. The interaction therefore resembles that of two hard spheres.
For *large impact parameters* ($b \to \infty$), the deflection function approaches zero. Since at large distances, the Lennard-Jones potential approaches zero, particles with large impact parameter barely interact, which leads to a behavior that resembles that of hard spheres.
For *intermediate impact parameters* we observe negative deflection angles χ, which is in stark contrast to the hard-sphere collisions. For decreasing impact parameter, the particle increasingly interacts with the attractive part of the potential, which leads to trajectories that wrap around the scattering center. This behavior is even more pronounced for lower energies of the particle E.

The differential cross section is obtained from $I(E,\chi) = b/\left|\frac{d\cos\chi}{db}\right|$ and is plotted below for $E \approx \epsilon$.

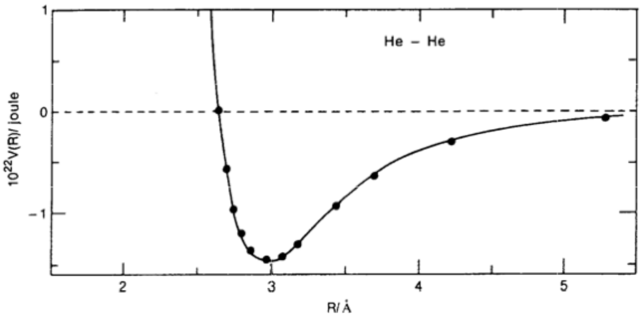


We see that for *small impact parameters* ($b \to 0, \chi \to \pi$), the differential cross section $I(\chi)$ approaches the constant hard sphere value $d^2/4$, which agrees with our discussion above. For *large impact parameters* ($b \to \infty,\ \chi \to 0$), the differential cross section diverges, since $\left|\frac{d\cos\chi}{db}\right| \to 0$ (dashed line). Similarly, we find a singularity (dashed line) at *intermediate impact parameters*, when the deflection function goes through a minimum at the so-called **rainbow angle** χ_r, so that $\left|\frac{d\cos\chi}{db}\right| \to 0$. The term "rainbow angle" alludes to mathematical similarities in light scattering from rain droplets that leads to the appearance of rainbows. The differential cross section can of course not become infinite. It turns out that the singularities in our calculation arise from the classical treatment of the collision process. A quantum mechanical treatment leads to the solid line shown above, in which the singularities are smoothed out by the quantum nature of the colliding particles.

By measuring differential cross sections, it is possible to deduce the intermolecular potential by means of the scattering theory derived above. We can see how this can be achieved if we integrate the equation for the differential cross section in a range of χ values in which $\chi(b)$ is monotonic, for example at angles larger than the rainbow angle.

$$\int_{\chi_0}^{\pi} I(E,\chi)|2\pi\sin\chi\, d\chi| = -\int_{b(\chi_0)}^{b(\pi)=0} 2\pi b db = \pi b(\chi_0)^2$$

This gives us a means to obtain the deflection function, which is connected to the potential $U(r)$ through the equations we derived above.



Interatomic potential of He–He. The solid curve represents experimental data; points are theoretical. [Adapted from A. L. Burgmans, J. M. Farrar, and Y. T. Lee, *J. Chem. Phys.*, *64*, 1345 (1976); unpublished computational results by B. Liu and A. D. McLean.]

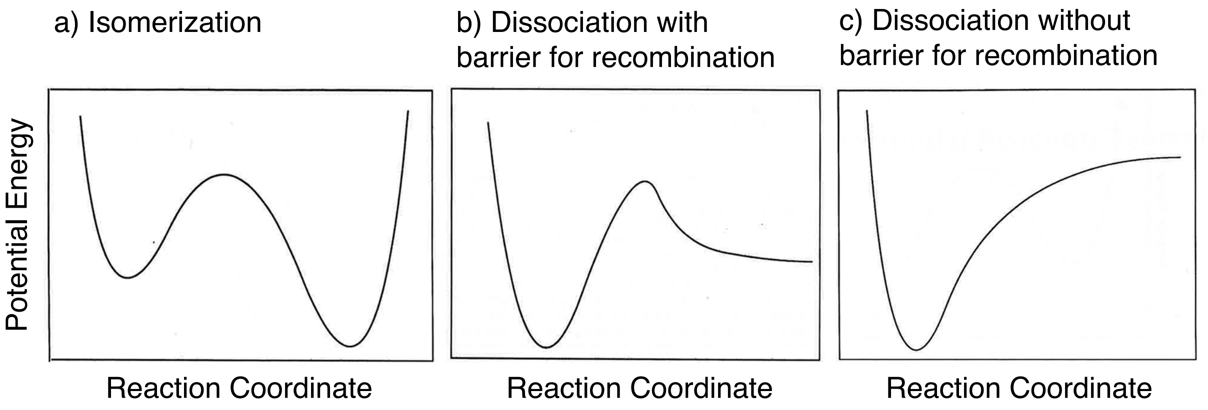
6 UNIMOLECULAR REACTION DYNAMICS

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 11. (Prentice Hall, 1989).

A unimolecular reaction follows the general equation

$$\mathrm{A}^* \rightarrow \text{products}$$

where the asterisk indicates that in order for a reaction to occur, the molecule A must possess a sufficiently high vibrational energy. We can distinguish three types of unimolecular reactions based on the features of the potential energy surface involved. This is illustrated below with examples for each type of potential energy surface.



$CH_3NC \rightarrow CH_3CN$ $\quad C_2H_5Cl \rightarrow HCl + C_2H_4$ $\quad C_2H_6 \rightarrow 2\ CH_3$

A key issue for understanding unimolecular reactions is the mechanism of how a molecule acquires sufficient energy to overcome the reaction barrier. In 1919, Perrin suggested that the molecules are energized by absorbing radiation from the walls of the reaction vessel. Such a dissociation mechanism has indeed been found to occur under special circumstances – for gaseous molecules at very low pressures. In the absence of collisions, the predominant dissociation mechanism involves the absorption of a large number of infrared photons that originate from black body radiation of the walls of the container, so that the molecules are excited to energies above the barrier.

However, at moderate gas pressures, unimolecular reaction rates are found to depend on pressure, which contradicts Perrin's hypothesis. Moreover, the rates do not depend on the surface to volume ratio of the container or the presence of absorbers. This suggests that the molecules are activated by collisions.

6.1 LINDEMANN-HINSHELWOOD THEORY OF THERMAL UNIMOLECULAR REACTIONS

This is the basis for the *Lindemann theory* (1922), which assumes that both activation and deactivation of molecules A occurs in a collision with a collision partner M:

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products}$$

Implicit in this model is the assumption that all $A^* + M$ collisions are “strong”, *i.e.*, they all de-energize the activated species A^*. Under this *strong collision assumption*, the deactivation rate k_{-1} can then be simply calculated from the gas-kinetic collision rate $z_{\mathrm{AM}} = \sigma_{\mathrm{AM}}\langle u_{\mathrm{AM}}\rangle\rho_{\mathrm{A}}\rho_{\mathrm{M}} = k_{-1}[\mathrm{A}][\mathrm{M}]$.

If we apply the steady-state approximation to the concentration $[\mathrm{A}^*]$, we obtain the overall rate R of the unimolecular rection:

$$R = k_{uni}[\mathrm{A}] = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$$

At low pressure ($[\mathrm{M}] \rightarrow 0$), we find

$$k_{uni} = k_0 = k_1[\mathrm{M}]$$

Here, the collisional activation is the rate-determining step, so that the rate k_{uni} becomes linearly dependent on the pressure.

At high pressure ($[\mathrm{M}] \rightarrow \infty$), we find instead that the rate becomes pressure independent:

$$k_{uni} = k_\infty = \frac{k_1 k_2}{k_{-1}}$$

Here, the activated and ground state species A^* and A are in a pre-equilibrium with

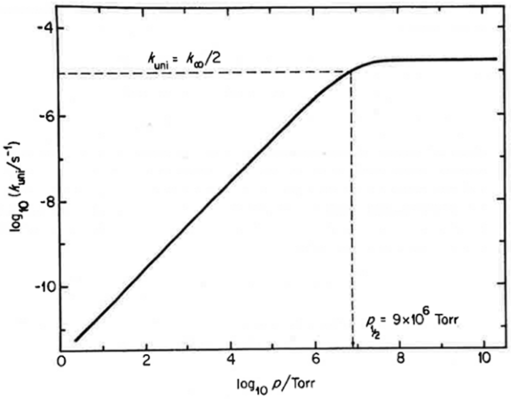
$$\frac{[\mathrm{A}^*]}{[\mathrm{A}]} = \frac{k_1}{k_{-1}}$$

so that the unimolecular rate constant k_{uni} simply becomes the probability of the molecule A being energized multiplied by the rate constant for the reaction k_2.

A log-log plot of the unimolecular rate constant, a so-called *Lindemann plot*

$$k_{uni} = \frac{k_\infty}{1 + \dfrac{k_\infty}{k_1[\mathrm{M}]}}$$

is shown below for the *cis*/*trans* isomerization of 2-butene at 496 °C.



The pressure $p_{\frac{1}{2}} \propto [\mathrm{M}]_{\frac{1}{2}} = \frac{k_\infty}{k_1}$ is marked at which $\frac{k_{uni}}{k_\infty} = \frac{1}{2}$.

While we have already derived the deactivation rate $k_{-1} = \sigma_{\text{AM}}\langle u_{\text{AM}}\rangle$ from the gas-kinetic collision rate z_{AM}, we will now also try to obtain expressions for the remaining two rate constants, k_1 and k_2. We could estimate the activation rate k_1 from the reactive-hard-spheres model, which predicts the rate at which collisions occur with a line-of-centers energy $E_\perp$exceeding a given threshold energy E^*

$$k(T) = \sigma_{\text{AM}}\langle u_{\text{AM}}\rangle e^{-\frac{E^*}{k_B T}} = k_{-1}e^{-\frac{E^*}{k_B T}}$$

where we assume that the threshold energy E^* is equal to the high-pressure activation energy E_0 of the reaction (with the steric factor $p = 1$).

One finds that this approach underestimates the experimentally found values for the activation rate k_1. In fact, the reactive hard spheres model neglects that the reactant molecule A already possesses a certain amount of internal energy that is stored in its vibrational degrees of freedom, which should lead to a higher activation rate k_1. The higher the number of vibrational degrees of freedom, the more energy the molecule stores at thermal equilibrium, and the higher k_1 should be. Based on this insight, *Hinshelwood* in 1926 derived the following expression for k_1, which improves the agreement with the experiment:

$$k_1 = \frac{k_{-1}}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$$

Here, s is the number of vibrational degrees of freedom of the molecule. We can see that for activation energies E_0 that are typically much higher than the thermal energy $k_B T$, the activation rate k_1 increases with the number of oscillators s. (Note that for large $s \gtrsim \frac{E_0}{k_B T}$, we actually find that the Hinshelwood expression predicts a decreasing rate. However, as we will see below, this is because the derivation makes the approximation that $s \ll \frac{E_0}{k_B T}$ in order to obtain a simple expression for k_1. Without this approximation, the rate is predicted to keep increasing with the number of oscillators s.)

In Hinshelwood's derivation, the ratio $\frac{k_1}{k_{-1}}$ is interpreted as the fraction of molecules exceeding the activation energy E_0 in the case of thermal equilibrium. As we have seen above, this is a good approximation at high pressure ([M] → ∞) where the energized molecules are in a pre-equilibrium with the ground-state molecules ($\frac{k_1}{k_{-1}} = \frac{[\text{A}^*]}{[\text{A}]}$). It is a more drastic approximation at low pressure, where energized molecules are formed in a single collision event that leads to a reaction before another collision can occur. We therefore have to make the *strong collision assumption* (as above for deenergizing collisions), *i.e.*, that individual collisions are strong enough to create a thermal population of activated molecules, as opposed to a ladder-climbing process involving multiple collisions to populate the highest energy levels.

In the following, we derive the expression for the probability $P(E)dE$ that in thermal equilibrium, a molecule has an energy between E and $E + dE$. With the approximation made above, we can relate this probability to the differential energizing rate dk_1 for populating molecular energy levels between E and $E + dE$

$$P(E)dE = \frac{dk_1}{k_{-1}} = \frac{1}{(s-1)!}\left(\frac{E}{k_B T}\right)^{s-1} e^{-\frac{E}{k_B T}}\left(\frac{dE}{k_B T}\right)$$

In thermal equilibrium, the probability $P(E)dE$ corresponds to a Boltzmann distribution for the vibrational degrees of freedom of the molecule, which we will describe as $3N-6$ $(3N-5)$ classical harmonic oscillators. In your quantum chemistry class, you have learnt that the energy levels of the harmonic oscillator are $E = \left(v + \frac{1}{2}\right)h\nu_i$, where ν_i is the eigenfrequency of the oscillator. The sum of states $G(E)$ of such an oscillator (*i.e.*, the number of levels with energies smaller than or equal to E) is approximately

$$G(E) = \frac{E}{h\nu_i}$$

In fact, this equation is exact, if we assume the oscillator to be classical, not quantum. The density of states $N(E) = \frac{dG(E)}{dE}$ (*i.e.*, the number of levels per unit energy) is then simply

$$N(E) = \frac{1}{h\nu_i}$$

The probability for such an oscillator to have an energy between E and $E + dE$ is given by the following Boltzmann expression:

$$P(E)dE = \frac{N(E)e^{-\frac{E}{k_BT}}dE}{\int_0^\infty N(E)e^{-\frac{E}{k_BT}}dE} = e^{-\frac{E}{k_BT}}dE$$

For s oscillators of energies E_i with $\sum_{i=1}^{s} E_i = E$, the sum of states becomes

$$G(E) = \int\limits_0^E \frac{dE_1}{h\nu_1} \int\limits_0^{E-E_1} \frac{dE_2}{h\nu_2} \dots \int\limits_0^{E-E_1-\dots-E_{s-1}} \frac{dE_s}{h\nu_s} = \frac{1}{\prod_{i=1}^{s} h\nu_i} \int\limits_0^E dE_1 \int\limits_0^{E-E_1} dE_2 \dots \int\limits_0^{E-E_1-\dots-E_{s-1}} dE_s$$

Let's rewrite the integral bounds

$$\int\limits_0^E dE_1 \int\limits_0^{E-E_1} dE_2 \dots \int\limits_0^{E-E_1-\dots-E_{s-1}} dE_s = \int\limits_0^{H_1} dE_1 \int\limits_0^{H_2} dE_2 \dots \int\limits_0^{H_s} dE_s$$

with $H_1 = E$ and $H_n = H_{n-1} - E_{n-1}$.

$$\begin{aligned}
\int\limits_0^{H_1} dE_1 \dots \int\limits_0^{H_{s-2}} dE_{s-2} \int\limits_0^{H_{s-1}} dE_{s-1} \int\limits_0^{H_s} dE_s &= \int\limits_0^{H_1} dE_1 \dots \int\limits_0^{H_{s-2}} dE_{s-2} \int\limits_0^{H_{s-1}} dE_{s-1}\, H_s \\
&= \int\limits_0^{H_1} dE_1 \dots \int\limits_0^{H_{s-2}} dE_{s-2} \int\limits_0^{H_{s-1}} dE_{s-1}\, (H_{s-1} - E_{s-1}) \\
&= \int\limits_0^{H_1} dE_1 \dots \int\limits_0^{H_{s-2}} dE_{s-2} \int\limits_{-H_{s-1}}^{0} d(E_{s-1} - H_{s-1}) - (E_{s-1} - H_{s-1}) \\
&= \int\limits_0^{H_1} dE_1 \dots \int\limits_0^{H_{s-2}} dE_{s-2} \frac{1}{2} H_{s-1}^2 = \int\limits_0^{H_1} dE_1 \int\limits_0^{H_2} dE_2 \dots \int\limits_0^{H_{s-2}} dE_{s-2} \frac{1}{2} (H_{s-2} - E_{s-2})^2 \\
&= \int\limits_0^{H_1} dE_1 \dots \frac{1}{3!} H_{s-2}^3 = \dots = \frac{1}{s!} E^s
\end{aligned}$$

We thus obtain

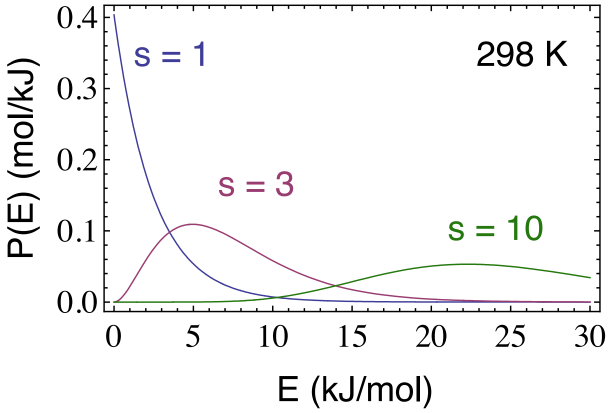
$$G(E) = \frac{E^s}{s!\prod_{i=1}^{s} h\nu_i}$$

and

$$N(E) = \frac{E^{s-1}}{(s-1)!\prod_{i=1}^{s} h\nu_i}$$

as well as[9]

$$P(E)dE = \frac{N(E)e^{-\frac{E}{k_BT}}dE}{\int_0^\infty N(E)e^{-\frac{E}{k_BT}}dE} = \frac{E^{s-1}e^{-\frac{E}{k_BT}}dE}{\int_0^\infty E^{s-1}e^{-\frac{E}{k_BT}}dE} = \frac{1}{(s-1)!}\left(\frac{E}{k_BT}\right)^{s-1} e^{-\frac{E}{k_BT}}\left(\frac{dE}{k_BT}\right)$$



In order to obtain k_1, we calculate the fraction of molecules with energy exceeding the activation energy E_0 through integration

$$\frac{k_1}{k_{-1}} = \int_{E_0}^{\infty} P(E)dE = \int_{E_0}^{\infty} \frac{1}{(s-1)!}\left(\frac{E}{k_BT}\right)^{s-1} e^{-\frac{E}{k_BT}}\left(\frac{dE}{k_BT}\right)$$

$$\underset{x=\frac{E}{k_BT}}{=} \frac{1}{(s-1)!}\int_{x_0=\frac{E_0}{k_BT}}^{\infty} (x)^{s-1}e^{-x}dx \quad \underset{y=x-x_0}{=} \quad \frac{e^{-x_0}}{(s-1)!}\int_0^\infty (y+x_0)^{s-1}e^{-y}dy$$

We carry out a binomial expansion for the term $(y+x_0)^{s-1}$ to find

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!}\sum_{j=0}^{s-1}\binom{s-1}{j}x_0^{s-1-j}\int_0^\infty y^j e^{-y}dy$$

We can evaluate this expression knowing that $\int_0^\infty y^j e^{-y}dy = \Gamma(j+1) = j!$

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[9] $\int_0^\infty x^{s-1}e^{-x}dx = \Gamma(s) = (s-1)!$

We can further simplify the expression if we assume that $x_0 = \frac{E_0}{k_B T} \gg s - 1$, *i.e.*, the activation energy E_0 is large compared to the thermal energy $k_B T$ multiplied by the number of oscillators s. This will be true for small molecules with typical activation energies. In this case, only the first term of the binomial expansion with $j = 0$ will be important, so that we obtain the expression stated initially above:

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} x_0^{s-1} = \frac{1}{(s-1)!} \left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$$

6.2 RICE-RAMSPERGER-KASSEL (RRK) THEORY

The RRK theory is a statistical theory that allows us to calculate the reaction rate constant k_2. It is obvious that this reaction rate constant should increase with the energy E of the activated molecule and thus be a function of the energy, $k_2 = k(E)$. Moreover, we expect that the rate constant should decrease when we increase the number of oscillators s because for a given energy E, the are more ways to distribute the energy between a larger number of oscillators. The probability for a sufficiently large amount of energy to be contained in the mode that leads to the reaction is thus lower.

We generalize the Lindemann-Hinshelwood mechanism to take into account that the activation and reaction rate constants both depend on the energy of the activated molecule. For an activated molecule A with an energy between E and $E + dE$, we obtain

$$\mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

$$\mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$

We obtain a differential unimolecular rate constant

$$dk_{uni} = \frac{k(E)\dfrac{dk_1}{k_{-1}}}{1 + \dfrac{k(E)}{k_{-1}[\mathrm{M}]}}$$

As discussed above, we assume that $\frac{dk_1}{k_{-1}} = P(E)dE$. Moreover, we note that $k_{-1}[\mathrm{M}]$ is the collision frequency ω of the reactant molecule.

$$dk_{uni} = \omega \frac{k(E)P(E)dE}{k(E) + \omega}$$

Upon integration, this gives the thermal unimolecular rate constant

$$k_{uni} = \omega \int_{E_0}^{\infty} \frac{k(E)P(E)dE}{k(E) + \omega}$$

The RRK theory assumes that the activated molecules of a specific energy $E \geq E_0$ form a *microcanonical ensemble*, *i.e.* all possible states of this energy are populated with equal probability.

Molecules with an energy of $E_0 + E'$ in the critical mode will dissociate (or isomerize) within one vibrational period of duration $1/\nu$, with ν the frequency of the critical oscillator. In other words, this fraction of molecules dissociates with a rate corresponding to ν.
Moreover, the theory assumes that even after some molecules have dissociated, the remaining molecules continue to form a microcanonical ensemble. This will only be the case if (1) the energy freely redistributes between all vibrational degrees of freedom (ergodic hypothesis) and (2) if this so-called intramolecular vibrational energy redistribution (IVR) occurs on a timescale much faster than the timescale of the reaction.

To derive the RRK rate constant $k(E)$, we first calculate the probability for a molecule to have an energy of $E_s \geq E_0$ in the critical mode by using the expressions derived above for density of states of a set of s classical oscillators.

The density of states $N(E, E_s \geq E_0)$ that have an energy of $E_s = E_0 + E'$ in the critical mode is the density of states of $s-1$ oscillators at a total energy of $E - E_0 - E'$ multiplied by the density of states of the critical oscillator at energy $E_s = E_0 + E'$ and integrated over all energies E'

$$N(E, E_s \geq E_0) = \int_0^{E-E_0} \frac{(E - E_0 - E')^{s-2}}{(s-2)! \prod_{i=1}^{s-1} h\nu_i} \cdot \frac{1}{h\nu_s} dE' = \frac{(E - E_0)^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i}$$

We divide this expression by the total density of states of s oscillators of total energy E

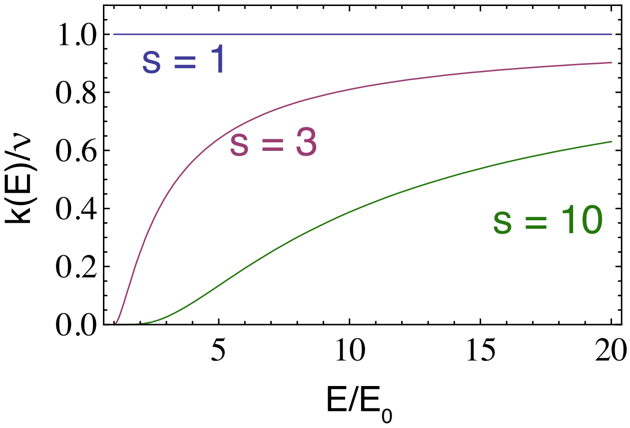
$$N(E) = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i}$$

to obtain the fraction of molecules that have an energy of $E_s \geq E_0$ in the critical mode

$$\frac{N(E, E_s \geq E_0)}{N(E)} = \left(\frac{E - E_0}{E}\right)^{s-1}$$

We obtain the classical RRK rate constant $k(E)$ by simply multiplying with the dissociation rate ν.

$$k(E) = \nu \left(\frac{E - E_0}{E}\right)^{s-1}$$

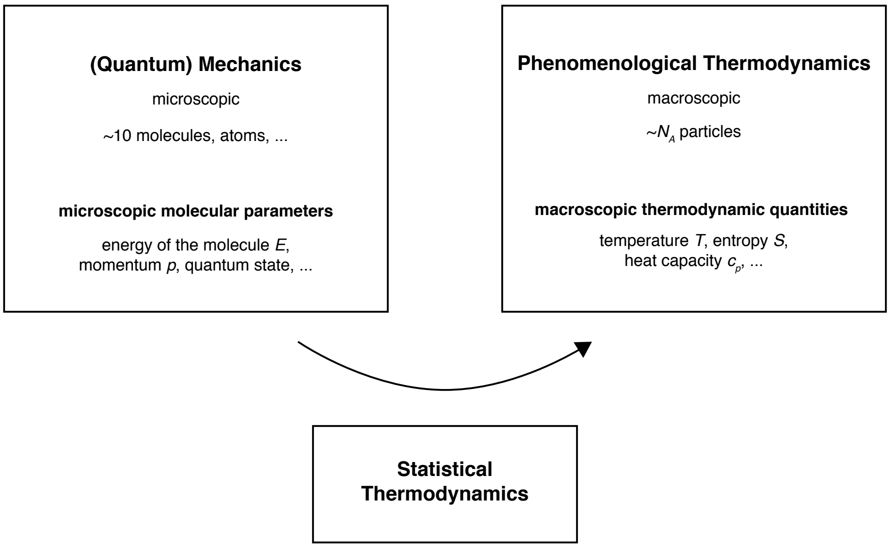


We are now able to calculate the unimolecular rate constant k_{uni} using just the variables s, ν, and E_0. The RRK treatment gives a reasonable agreement with experiments. Shortcomings arise from the classical treatment of the vibrations of the molecule. Moreover, the Arrhenius prefactor ν, which in the

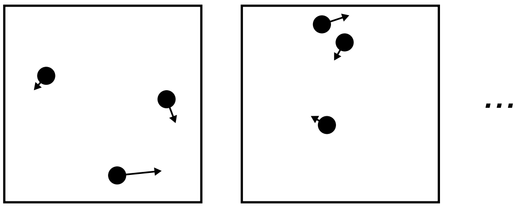
RRK model corresponds to a vibrational frequency ($10^{13} – 10^{14}$ s^{-1}) underestimates experimental values, which are usually larger than 10^{14} s^{-1}. Such discrepancies are overcome by the RRKM theory, which is a microcanonical transition state theory.

7 BASIC CONCEPTS OF STATISTICAL THERMODYNAMICS

This chapter provides a brief overview of some basic concepts of statistical thermodynamics that we will subsequently apply in the derivation of Transition State Theory. Statistical thermodynamics is based on the insight that macroscopic thermodynamic quantities ultimately arise from the properties of individual molecules, which are described by quantum mechanics. Knowing the properties of molecules, we can use statistical thermodynamics to derive macroscopic thermodynamic quantities. Since thermodynamics deals with large ensembles of molecules, we can understand these quantities to be averages of molecular parameters.



As an example, let us consider a container filled with a monoatomic gas. We can use macroscopic parameters, such as the temperature T, to describe the *macrostate* of this large ensemble of gas molecules. At the same time, many different *microstates* exist that each correspond to this temperature. To see this, consider that each gas molecule has 3 parameters that describe its position as well as three that describe its momentum, giving a total of $6N$ parameters $\{x_i, p_i\}$ for all N gas molecules. As the gas molecules are in motion, these parameters will assume different values at different points in time. Nevertheless, these different microstates that the gas can assume all have the same temperature.



Statistical thermodynamics makes two assumptions about these microstates.

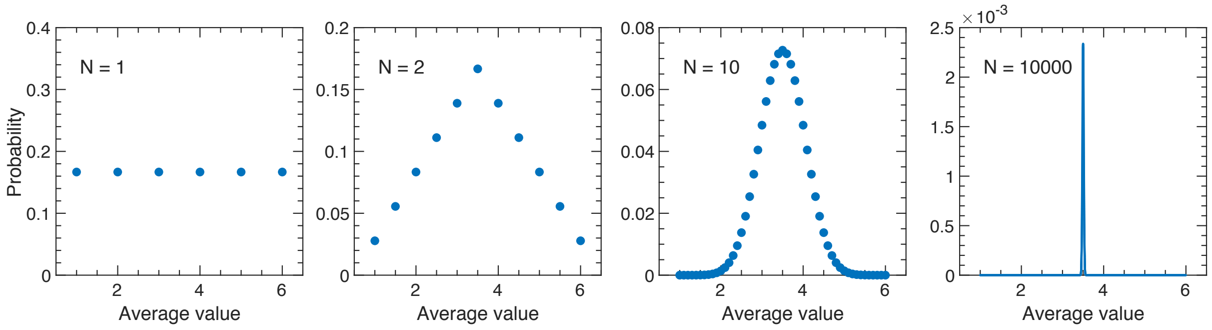
Postulate 1. The ergodic hypothesis states that over a sufficiently long period of time, a given system will assume all possible microstates. In other words, if we start the system in one microstate, the system will explore all other microstates that are possible for the given starting parameters. A consequence of this postulate is that the time average of some observable M is equal to the ensemble average.

$$\langle M \rangle_{t\to\infty} = \langle M \rangle_{n\to\infty}$$

Postulate 2. According to the principle of equal *a priori* probabilities, all microstates have the same probability. Taken together with Postulate 1, this means that the system will spend equal amounts of time in each microstate.

Under these assumptions, we can determine which macrostate the system will assume under given conditions simply by determining the *statistical weight W* of this macrostate, *i.e.* the number of microstates that correspond to that macrostate. The macrostate with the highest number of microstates will be the most probable. For a large number of molecules, this is the only macrostate we need to consider, as it will be vastly more probable than any other state. This is a consequence of the law of large numbers.

As an example, to illustrate this point, consider rolling N dices, where every dice represents a particle or molecule. We are interested in a macroscopic property of the system, say the average number $\langle A \rangle$ shown by the dices. The probability of different outcomes is shown below.



For $N = 2$ dices, we see that the macrostate with $\langle A \rangle = 3.5$ is the most probable, with six different microstates $\{(1,6),(2,5),(3,4),(4,3),(5,2),(6,1)\}$ corresponding to this outcome. For $N = 10$, the probability distribution becomes more peaked, and for $N = 10000$, the macrostate $\langle A \rangle = 3.5$ is considerably more likely than other macrostates. For $N \to \infty$, we obtain a delta function. By analogy, we can conclude that in order to describe the average properties of a large ensemble of molecules, we only need to consider the most probable macrostate.

7.1 DERIVATION OF THE BOLTZMANN DISTRIBUTION

An important macroscopic property of an ensemble is the distribution of energy within it. Assume that the N molecules of the ensemble are distributed of the energy levels $\{E_i\}$ and that N_i molecules have the energy E_i, with

$$N = \sum_i N_i$$

and

$$E = \sum_i E_i \, N_i$$

where the energy E is the total energy of the ensemble. If we are studying a microcanonical ensemble, this energy is a fixed quantity, since in a microcanonical ensemble, the particle number N, the volume V, and the total energy of the ensemble E are given. In a canonical ensemble, the particle number N, the volume V, and the temperature T are given. Here, the total energy is a function of the temperature, $E(T)$.

For the statistical weight W of a given macrostate, we find

$$W = \frac{N!}{\prod_i N_i!}$$

We obtain this result if we consider that there are $N!$ ways of sorting the N particles into the different energy levels of a given macrostate. However, it does not matter how the N_i molecules of a given energy E_i are sorted. Since there are $N_i!$ ways of sorting these molecules, we divide by $N_i!$ for every energy level E_i.

We seek to find the macrostate with the highest statistical weight W. In other words, we want to find the maximum of W, where the following condition must hold

$$d \ln W = \sum_i \frac{\partial \ln W}{\partial N_i} dN_i = 0$$

Here, we choose to find the maximum of $\ln W$, which is equivalent to finding the maximum of W, but facilitates the math in the following.

We have to keep in mind that we have to find this maximum under two constraints, namely that the number of particles is fixed ($N = \sum_i N_i$) as well as the total energy ($E = \sum_i E_i$). In order to satisfy these constraints, we choose the method of *Lagrange multipliers* to find the maximum. We first write these to constraints in differential form

$$dN = \sum_i dN_i = 0 \qquad | \cdot \alpha$$

$$dE = \sum_i E_i \, dN_i = 0 \qquad | \cdot \beta$$

and then multiply them with the Lagrange multipliers α and β, respectively. Finally, we add all three equations to obtain

$$\sum_i \frac{\partial \ln W}{\partial N_i} dN_i - \sum_i \alpha \, dN_i - \sum_i \beta \, E_i \, dN_i = 0$$

After rearrangement, we obtain

$$\sum_i \left(\frac{\partial \ln W}{\partial N_i} - \alpha - \beta \, E_i \right) dN_i = 0$$

This equation can only hold if

$$\frac{\partial \ln W}{\partial N_i} - \alpha - \beta\, E_i = 0 \qquad \text{for all } i.$$

We use Stirling's approximation[10] to simplify the expression for $\ln W$

$$\ln x! = x \ln x - x \qquad \text{for all } x \gg 1$$

so that

$$\ln W = \ln N! - \sum_i N_i! \approx N \ln N - N - \left(\sum_i N_i \ln N_i - \sum_i N_i \right)$$

With $\sum_i N_i = N$, we obtain

$$\ln W = N \ln N - \sum_i N_i \ln N_i$$

so that

$$\frac{\partial \ln W}{\partial N_i} = \frac{\partial (N \ln N)}{\partial N_i} - \frac{\partial}{\partial N_i}(N_i \ln N_i) = -\ln N_i - 1 \approx -\ln N_i$$

Finally, we obtain

$$\ln N_i = -\alpha - \beta\, E_i$$

or

$$N_i = e^{-\alpha} e^{-\beta E_i}$$

Using the method of Lagrange multipliers, we have thus obtained an expression for the most probable number of molecules N_i that occupy energy level E_i. We still have not determined the multipliers α and β, which we will do in the following. We can eliminate α by calculating the population fraction in a given level i

$$\frac{N_i}{N} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{Q}$$

Here, we have defined the *partition function* Q with

$$Q = \sum_i e^{-\beta E_i}$$

---

[10] $\ln x! = \ln 1 + \ln 2 + \cdots \approx \int_0^x \ln x\, dx = x \ln x |_0^x - x|_0^x = x \ln x - x$, where we have used partial integration in the last step.

We are left to determine β. We can for example do this by comparing with an expression that we have obtained in the context of the kinetic theory of gases (section 4.1). There, we found that the ideal gas law can be related to the average square of one velocity component of the gas molecules

$$pV = k_B NT = Nm\langle u_x^2 \rangle$$

We can now determine the average square of one velocity component $\langle u_x^2 \rangle$ using the distribution function we just obtained

$$\langle u_x^2 \rangle = \frac{\int_{-\infty}^{\infty} u_x^2 e^{-\beta\frac{1}{2}mu_x^2} du_x}{\int_{-\infty}^{\infty} e^{-\beta\frac{1}{2}mu_x^2} du_x} = \frac{1}{\beta m}$$

so that we find $\beta = 1/\, k_B T$ and

$$\frac{N_i}{N} = \frac{e^{-\frac{E_i}{k_B T}}}{Q}$$

We have thus obtained the familiar *Boltzmann distribution*.

In the case of energy levels with degeneracy g_i, we can easily see that the distribution becomes

$$\frac{N_i}{N} = \frac{g_i\, e^{-\frac{E_i}{k_B T}}}{Q}$$

with

$$Q = \sum_i g_i\, e^{-\frac{E_i}{k_B T}}$$

7.2 PARTITION FUNCTIONS

We have seen that in the derivation of the Boltzmann distribution, the partition function Q naturally occurred. In order to develop a better understand of the meaning of the partition function, let us write it out with all energies referenced to the lowest energy level of the system, which we set to have zero energy $E_0 = 0$. In this case,

$$Q = \sum_i g_i\, e^{-\frac{E_i}{k_B T}} = g_0 + g_1 e^{-\frac{E_1}{k_B T}} + \cdots$$

We can see that at $T = 0$ K, only the ground state is populated $Q = g_0$. In other words, the system has access to only g_0 energy levels. At higher temperatures, higher energy states can be partially populated and $Q > g_0$. The exponential terms lead to values smaller than one and therefore to partial populations of the upper energy levels. Knowing that $k_B T$ corresponds to the thermal energy a system has available, we can interpret the partition function to be a measure of the number of states that are accessible to a system at a given temperature.

Importantly, will see in the following that the partition function of a system allows us to derive all thermodynamic quantities. Moreover, it is a crucial component to understanding Transition State Theory.

Let us consider the partition function of one molecule. As you have learnt in your Quantum Chemistry class, the energy of a molecule is a sum of translational, rotational, vibrational, and electronic energy.

$$\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec}$$

At low enough temperatures, we can usually neglect the electronic part as only the electronic ground state is populated. In this case, we can write down the *molecular partition function* q as follows.

$$q = \sum_i g_i \, e^{-\frac{\epsilon_i}{k_B T}} = \sum_{ijk} g_{trans,i} g_{rot,j} g_{vib,k} \, e^{-\frac{\epsilon_{trans,i} + \epsilon_{rot,j} + \epsilon_{vib,k}}{k_B T}} = q_{trans} q_{rot} q_{vib}$$

We see that the molecular partition function is a product of a translational, a rotational, and a vibrational partition function.

With knowledge of the energy levels of the particle of the box, the rigid rotor, and the harmonic oscillator, we can derive approximate expression for the translational, rotational, and vibrational partition functions, as shown in Appendix B.

We can also derive the *partition function of an ensemble* of N molecules that we will here assume to be non-interacting, *i.e.* the energy levels of a molecule that is part of the ensemble are identical to those of an isolated molecule. A given energy E_j that the ensemble can assume is the sum of the energies ϵ_j^i of all the molecules of the ensemble

$$E_j = \sum_i \epsilon_j^i$$

For the partition function of the ensemble, we obtain

$$Q = \sum_j g_j \, e^{-\frac{E_j}{k_B T}} = \sum_j \prod_i g_j^i e^{-\frac{\epsilon_j^i}{k_B T}} = \prod_i \sum_j g_j^i e^{-\frac{\epsilon_j^i}{k_B T}} = \prod_i q = q^N$$

We see that the partition function of an ensemble of N non-interacting molecules is equal to the partition function of one molecule to the power of N.

In a crystal, where each molecule has a fixed position, one can distinguish the individual molecules. This is not the case in a gas. For N indistiguishable molecules, we obtain instead

$$Q = \frac{q^N}{N!}$$

where we take into account that for each energy of the ensemble, there are $N!$ combinations that lead to this energy, which we cannot distinguish.

7.3 THERMODYNAMIC FUNCTIONS

If we know the partition function of an ensemble, we can derive all thermodynamic functions from it. In the following, we will go through the most important.

Internal energy U:

$$U = N \cdot \langle \epsilon \rangle = N \cdot \frac{\sum_i \epsilon_i g_i \, e^{-\frac{\epsilon_i}{k_B T}}}{\sum_i g_i \, e^{-\frac{\epsilon_i}{k_B T}}} = N \cdot \frac{k_B T^2 \frac{\partial q}{\partial T}}{q} = N k_B T^2 \frac{\partial \ln q}{\partial T} = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

Heat capacity c_v:

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{\partial}{\partial T}\left(k_B T^2 \frac{\partial \ln Q}{\partial T}\right) = 2 k_B T \frac{\partial \ln Q}{\partial T} + k_B T^2 \frac{\partial^2 \ln Q}{\partial T^2}$$

Entropy S:

$$dS = \frac{dQ^*}{T} = \frac{c_v dT}{T}$$

where Q^* refers to heat, not the partition function.

$$S = \int_0^S dS = \int_0^T dT \, 2k_B \frac{\partial \ln Q}{\partial T} + k_B T \frac{\partial^2 \ln Q}{\partial T^2} = 2k_B \ln Q + k_B T \frac{\partial \ln Q}{\partial T} - k_B \ln Q$$
$$= k_B T \frac{\partial \ln Q}{\partial T} + k_B \ln Q = \frac{U}{T} + k_B \ln Q$$

Helmholtz free energy A:

$$A = U - TS = -k_B T \ln Q$$

Pressure p:

$$dA = dU - TdS - SdT = -SdT - pdV$$

where we have used

$$dU = TdS - pdV$$

It follows that

$$p = -\frac{\partial A}{\partial V} = k_B T \frac{\partial \ln Q}{\partial V}$$

Enthalpy H:

$$H = U + pV = k_B T^2 \frac{\partial \ln Q}{\partial T} + k_B T \frac{\partial \ln Q}{\partial V} V = k_B T \left[\frac{\partial \ln Q}{\partial \ln T} + \frac{\partial \ln Q}{\partial \ln V}\right]$$

Gibbs free energy G:

$$G = A + pV = -k_B T \ln Q + k_B T \frac{\partial \ln Q}{\partial \ln V}$$

7.4 EQUILIBRIUM CONSTANTS OF GAS PHASE REACTIONS

Here, we will express the equilibrium constant for a gas phase reaction in terms of partition functions. In equilibrium,

$$\sum_i \nu_i \mu_i = 0$$

where ν_i is the stoichiometric coefficient of compound i (negative for reactants and positive for products), and μ_i is the chemical potential

$$\mu_i = \left(\frac{\partial G_i}{\partial n_i}\right)_{p,T,n_j \neq n_i} = \left(\frac{\partial A_i}{\partial n_i}\right)_{V,T,n_j \neq n_i}$$

The Helmholtz free energy A_i of an ideal gas with N_i non-distinguishable particles is

$$A_i = -k_B T \ln Q_i = -k_B T \ln \frac{q_i^{N_i}}{N_i!} = -k_B T N_i \ln q_i + k_B T N_i \ln N_i - k_B T N_i$$
$$= -n_i R T \ln \frac{q_i}{n_i N_A} - R n_i T$$

where N_A is Avogadro's constant. Consequently,

$$\mu_i = \left(\frac{\partial A_i}{\partial n_i}\right)_{V,T,n_j \neq n_i} = -RT \ln \frac{q_i}{N_i}$$

Finally, we have to introduce one more modification to the partition functions. When we write

$$q_i = \sum_j g_j \, e^{-\frac{\epsilon_{ij}}{k_B T}}$$

the energies ϵ_{ij} are referenced to the ground state energy of the molecule i. However, in an expression dealing with several different reactants and products, we have to introduce a common energy scale. We do this by referencing all molecules to the energy, at which reactants and products are entirely dissociated into atoms, with the corresponding atomization energy of species i denoted by ϵ_{id}. It is this atomization energy that we substract from the molecular energies, so that we obtain the modified partition function q_{id}

$$q_{id} = \sum_j g_j \, e^{-\frac{\epsilon_{ij} - \epsilon_{id}}{k_B T}} = e^{\frac{\epsilon_{id}}{k_B T}} q_i$$

Finally, we can write

$$\sum_i \nu_i \mu_i = \sum_i -RT \ln \frac{q_i^{\nu_i} e^{\frac{\nu_i \epsilon_{id}}{k_B T}}}{N_i^{\nu_i}} = -RT \ln \prod_i \frac{q_i^{\nu_i} e^{\frac{\nu_i \epsilon_{id}}{k_B T}}}{N_i^{\nu_i}} = 0$$

Rearrangement gives the equilibrium constant K_N

$$K_N = \prod_i N_i^{\nu_i} = \prod_i q_i^{\nu_i} \cdot e^{-\frac{\Delta U_0}{RT}}$$

where

$$\Delta U_0 = N_A \sum_i \nu_i \epsilon_{id}$$

is the reaction energy at 0 K. Note that the equilibrium constant K_N is defined in terms of numbers N_i of the different species. In order to obtain the more familiar equilibrium constant K_c that is defined in terms of molar concentrations c_i, we have to divide each number N_i by Avogadro's contant N_A as well as the reaction volume V.

$$K_c = \prod_i c_i^{\nu_i} = \prod_i \left(\frac{N_i}{N_A V}\right)^{\nu_i} = \prod_i \left(\frac{q_i}{N_A V}\right)^{\nu_i} \cdot e^{-\frac{\Delta U_0}{RT}} = (N_A V)^{-\sum_i \nu_i} \prod_i q_i^{\nu_i} \cdot e^{-\frac{\Delta U_0}{RT}}$$

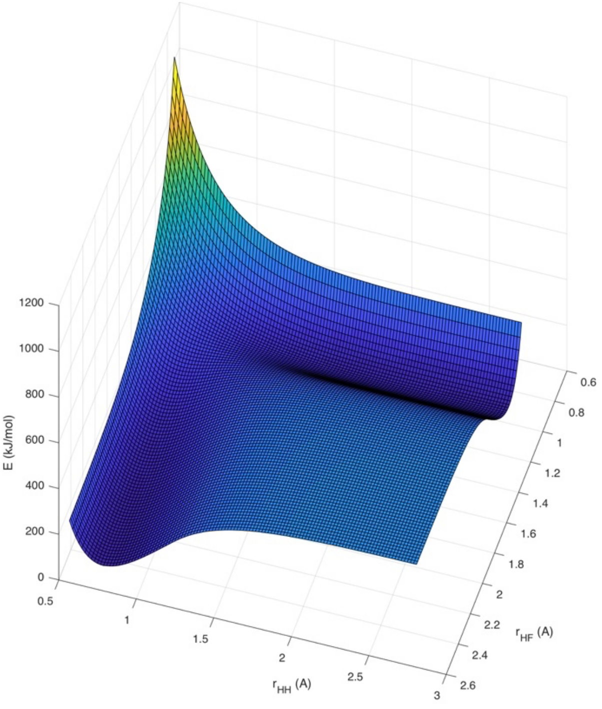
8 TRANSITION STATE THEORY

Steinfeld, J. I., Francisco, J. S. & Hase, W. L. *Chemical Kinetics and Dynamics* Ch. 10. (Prentice Hall, 1989).

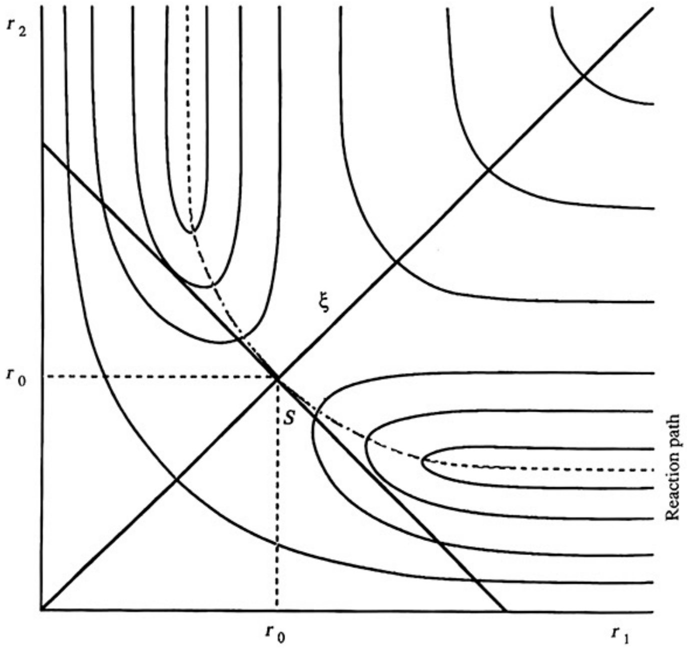
Transition State Theory predicts the rate constants of reactions based on the statistical properties of the system. The basic assumption of the theory is that the transition state of the reaction is in thermal equilibrium with the reactants, so that statistical thermodynamics can be used to derive a simple expression for the thermal rate constant. Since Transition State Theory is based on a statistical picture, it neglects any microscopic details of the reaction and will fail if those are important. This may for example be the case if under the experimental conditions, the reactants do not form a statistical ensemble. In this case, only detailed (quantum) dynamics simulations would be able to provide an accurate picture.

8.1 MOTION ON THE POTENTIAL ENERGY SURFACE

As you have learnt in your Quantum Chemistry course, the Born-Oppenheimer approximation allows us to separate the electronic and nuclear motion. The nuclei can then be thought of as moving within a potential that is created by the electron cloud, which instantaneously rearranges when the nuclear positions change. An example of a calculated potential energy surface is shown below for the reaction of H_2 with an F atom. This system has $3N - 6 = 3$ vibrational degrees of freedom. However, in order to be able to display the surface, we restrict the nuclei to a linear collision geometry. This leaves only two coordinates, the hydrogen-hydrogen distance (r_{HH}) and the hydrogen-fluorine distances (r_{HF}).



The contour plot below illustrates the salient features of a potential energy surface, here that of the reaction of H_2 with an H atom, also in linear geometry. Since this is a degenerate reaction, the surface is symmetric with respect to the diagonal. The two hydrogen-hydrogen distances are labeled r_1 and r_2.



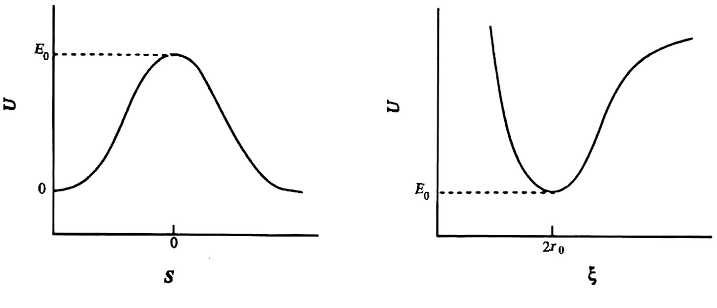
The dashed line marks the *minimum energy path* leading from the configuration H_2 … H to the configuration H … H_2. Products and reactants are separated by the *transition state*, a saddle point of the potential energy surface that lies on the minimum energy path. For the H_2 … H system, the transition state is symmetric with $r_1 = r_2 = r_0$. If we perform a normal mode analysis at the saddle point, we find that one of the normal modes s corresponds to motion along the minimum energy path

$$s = r_1 - r_2$$

and the other normal mode ξ to motion orthogonal to the minimum energy path

$$\xi = r_1 + r_2$$

The potential U as a function of s and ξ is shown below.



We can see that at the transition state, the minimum energy path has a maximum, while the orthogonal coordinate shows a minimum. In general, the transition state is a saddle point, which is a maximum along the reaction coordinate (the minimum energy path), and a minimum along all other normal modes.

A normal mode analysis at the transition state therefore reveals one imaginary frequency, which belongs to the normal mode that describes motion along the minimum energy path. To see this, remember that for a harmonic oscillator, the angular frequency is $\omega = \sqrt{\frac{k}{\mu}}$, with $k = \frac{d^2U}{dx^2}$, where μ is the reduced mass and x the coordinate of the oscillator. All other $3N - 7$ frequencies are real and correspond to vibrations of the other normal modes.

8.2 POSTULATES AND DERIVATION

Transition State Theory (Eyring, Evans, and Polanyi) makes two basic assumptions, namely that electronic and nuclear motion can be separated as discussed above (Born-Oppenheimer approximation) and that the reactant molecules are distributed among their energy states according to the Boltzmann distribution.

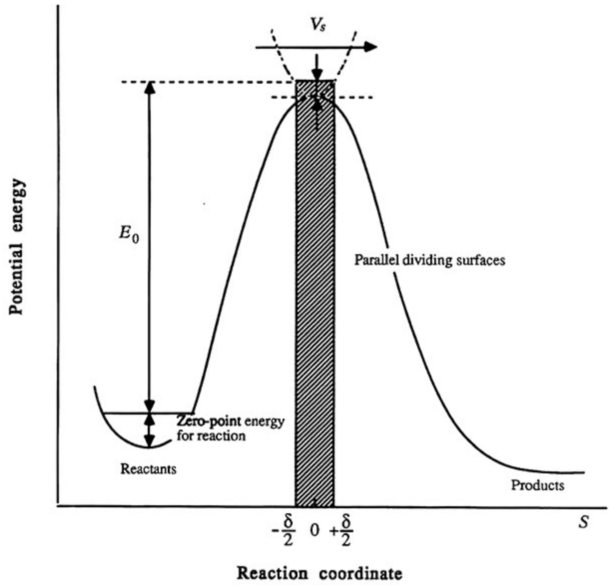
The theory uses a simple physical picture of an elementary reaction, say between reactants A and B, which proceed through a transition state $\mathrm{X}^\ddagger$ to form products

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X}^\ddagger \rightarrow \mathrm{products}$$

Transition State Theory makes the following specific assumptions.

1) No recrossing. Reactants that have crossed the transition state $\mathrm{X}^\ddagger$ in the direction of products cannot turn around and reform reactants. Similarly, if reactants and products are in equilibrium, then the products that have crossed the transition state in the direction of the reactants, cannot turn around to reform products.

The sketch below depicts the potential energy as a function of the reaction coordinate s or the minimum energy path. We define a small region on top of the barrier between two parallel *dividing surfaces* that are orthogonal to the reaction path and that are located at $s = -\frac{\delta}{2}$ and $s = \frac{\delta}{2}$. Note that these surfaces are $3N - 7$ dimensional. We consider all molecules between these two surfaces as transition states. Those outside these surfaces are either reactants or products.



2) Quasi-equilibrium hypothesis. The transition states are distributed among their states according to the Boltzmann distribution, even if there is no equilibrium between reactants and products. It can be shown that this second assumption is not strictly necessary, but that only the first assumption is fundamental to the theory.

If reactants and products are in equilibrium, we will have both transition states moving forward to give products as well as those moving backwards to form reactants. We denote their concentrations as $N_f^\ddagger$ and $N_b^\ddagger$, respectively. At equilibrium, the number of transitions states moving forward must equal the number of transition states moving backwards, $N_f^\ddagger = N_b^\ddagger$. Moreover, the total concentration of transition states is $N^\ddagger = N_f^\ddagger + N_b^\ddagger = 2N_f^\ddagger$.

Under the assumption of quasi-equilibrium

$$N^\ddagger = K^\ddagger[\mathrm{A}][\mathrm{B}]$$

where $K^\ddagger$ is the equilibrium constant for the formation of the transition state. Moreover, we can calculate the concentration of the forward moving transition states

$$N_f^\ddagger = \frac{N^\ddagger}{2} = \frac{1}{2}K^\ddagger[\mathrm{A}][\mathrm{B}]$$

We can derive this equilibrium constant $K^\ddagger$ from statistical thermodynamics (Section 7.4). For a gas-phase reaction,

$$K^\ddagger = \frac{Q_{tot}^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

where the partition functions of the reactants, Q_A and Q_B, as well as that of the transition state $Q_{tot}^\ddagger$ are defined as the molecular partition functions q_i divided by Avogadro's number N_A and the reaction volume V.

$$Q_i = \frac{q_i}{N_A V}$$

The energy E_0, which we defined as the reaction energy at 0 K (Section 7.4), corresponds to the difference in zero-point energies between reactants and the transition state, as indicated in the sketch above.

Now that we have derived the concentration of the forward moving transition states $N_f^\ddagger$, we just need an expression for the forward reaction rate $k^\ddagger$. The product of both gives the rate of the reaction

$$R = k^\ddagger N_f^\ddagger$$

which divided by $[\mathrm{A}][\mathrm{B}]$ gives the rate constant of the reaction

$$k_{\mathrm{TST}} = k^\ddagger \frac{N_f^\ddagger}{[\mathrm{A}][\mathrm{B}]} = \frac{1}{2}k^\ddagger K^\ddagger$$

In order to calculate the forward reaction rate, Transition State Theory makes one more assumption.

3) Classical motion along the reaction coordinate. At the transition state, motion along the reaction coordinate may be separated from the other coordinates and may be treated classically. Note that by treating the motion classically, quantum effects are specifically neglected, such as tunneling through the barrier or quantum reflections, which you have encountered in your Quantum Chemistry course. This leads to some of the shortcomings of Transition State Theory.

The average time δt for a transition state to traverse the dividing surfaces is

$$\delta t = \frac{\delta}{\langle v_s \rangle}$$

where $\langle v_s \rangle$ is the average velocity in the reaction coordinate s. Under the assumption of quasi-equilibrium, we can calculate this average velocity from a Boltzmann distribution.

$$\langle v_s \rangle = \frac{\int_0^\infty v_s e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s}{\int_0^\infty e^{-\frac{\mu_s v_s^2}{2k_B T}} dv_s} = \sqrt{\frac{2k_B T}{\pi \mu_s}}$$

Here, μ_s is the reduced mass of the reaction coordinate s. Note that we integrate from zero to infinity because we only consider forward moving transition states. Moreover, note that we have already performed this calculation in Section 4.2 in the context of the kinetic theory of gases and that the expression obtained corresponds the mean absolute velocity of a one-dimensional ideal gas. We obtain

$$k^{\ddagger} = \frac{1}{\delta t} = \frac{\langle v_s \rangle}{\delta} = \frac{1}{\delta} \sqrt{\frac{2k_B T}{\pi \mu_s}}$$

which gives us the rate constant of the reaction

$$k_{\text{TST}} = \frac{1}{2} k^{\ddagger} K^{\ddagger} = \frac{1}{2\delta} \sqrt{\frac{2k_B T}{\pi \mu_s}} \frac{Q_{tot}^{\ddagger}}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

Since we have assumed that we can separate the translational motion in the reaction coordinate from all other degrees of freedom, the total energy must be a sum of the translational energy of the reaction coordinate and the vibrational energy contained in all other modes. In this case, the total partition function of the transition state $Q_{tot}^{\ddagger}$ can be written as the product of the partition function of the reaction coordinate Q_s and that of the remaining modes $Q^{\ddagger}$.

$$Q_{tot}^{\ddagger} = Q_s Q^{\ddagger}$$

In chapter 7, we have encountered several similar cases. For example, the energy of a particle in a three-dimensional box is the sum of the energies of three separate particles in one-dimensional boxes. Therefore, the partition function can be written as the product of the partition functions of three particles in one-dimensional boxes.

Here, we can easily see that the partition function of the reaction coordinate Q_s must be the translational partition function of a particle of mass μ_s in a one-dimensional box of length δ (Appendix B).

$$Q_s = \frac{\delta}{h} \sqrt{2\pi \mu_s k_B T}$$

After substitution, we obtain the Transition State Theory rate constant

$$k_{\mathrm{TST}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}}$$

Note that both the distance of the dividing surfaces δ as well as the reduced mass of the reaction coordinate μ_s have disappeared from the final equation. In order to determine the Transition State Theory rate constant k_{TST}, we need to calculate the partition functions of both the reactants and the transition state. In particular, we must have knowledge of the vibrational frequencies and the rotational constants (or moments of inertia). For the transition state, such information is usually hard to obtain and is therefore frequently taken from quantum chemical calculations.

In the expression for k_{TST} given above, $\frac{k_B T}{h}$ is called the *frequency factor* and has a value of $6.25 \cdot 10^{12}\ \mathrm{s}^{-1}$ at 300 K. It is of the same order of magnitude as the encounter frequency of molecules in liquids and comparable to the vibrational frequency of slow molecular vibrations (300 K corresponds to 200 cm^{-1}), but too low if compared to the timescale of a molecular collision.

Finally, we can relate the energy E_0 to the Arrhenius activation energy E_a. According to Tolman's theorem, the activation energy of a reaction E_a is equal to the difference between the mean energy of the reacting molecules $\langle E_R \rangle$ and the mean energy of all molecules $\langle E \rangle$.

$$E_a = \langle E_R \rangle - \langle E \rangle$$

In the context of Transition State Theory, the mean energy of the reacting molecules $\langle E_R \rangle$ is the sum of the energy E_0 and the mean energy of the transition state.

Transition State Theory successfully describes a large number of thermal rate constants. Its shortcomings arise from the classical treatment of motion through the transition state. Quantum mechanically, the transition state cannot be treated as a definite configuration of nuclei moving at a given velocity. Instead, the uncertainty principle demands that the transition state is delocalized in space. Similarly, it cannot have an infinitesimally short lifetime at a finite energy uncertainty. We also assume that the potential of the reaction path is flat when we treat the motion along the reaction path as a free translation. This is not the case. Instead, the reaction path leads over a barrier, so that tunneling and quantum reflections can occur, which a classical theory cannot account for. Finally, the reaction path is usually curved, so that it cannot be decoupled from the other degrees of freedom. Therefore, it is not possible to factor the partition function of the transition state into one for the translation and one for the other degrees of freedom.

8.3 THERMODYNAMIC FORMULATION

We can reformulate the Transition State Theory rate constant in thermodynamic terms, so that we do not need to deal with partition functions, which is sometimes more convenient. Above, we have seen that

$$k_{\mathrm{TST}} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q_A Q_B} e^{-\frac{E_0}{k_B T}} = \frac{k_B T}{h} K^\ddagger$$

with the equilibrium constant for the formation of the transition state $K^\ddagger$. We can associate this equilibrium constant with a molar standard Gibbs free energy

$$\Delta G^{\ddagger o} = -RT \ln K^\ddagger$$

to obtain

$$k_{\mathrm{TST}} = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger o}}{RT}} = \frac{k_B T}{h} e^{\frac{\Delta S^{\ddagger o}}{R}} e^{-\frac{\Delta H^{\ddagger o}}{RT}}$$

Here, the superscript “o” refers to the standard state. We obtain the rate constant in terms of a standard enthalpy and entropy of activation. We can compare this equation to the Arrhenius equation

$$k = A e^{-\frac{E_a}{RT}}$$

with the activation energy

$$E_a = RT^2 \frac{d \ln k}{dT}$$

For the Transition State Theory rate constant, we obtain

$$RT^2 \frac{d \ln k_{TST}}{dT} = RT + RT^2 \frac{d \ln K^{\ddagger}}{dT}$$

Furthermore, the Gibbs-Helmholtz equation tells us that

$$\frac{d \ln K^{\ddagger}}{dT} = \frac{\Delta E^{\ddagger o}}{RT^2}$$

so that

$$E_a = RT + \Delta E^{\ddagger o}$$

We can relate this to the activation enthalpy $\Delta H^{\ddagger o}$, assuming constant pressure

$$\Delta H^{\ddagger o} = \Delta E^{\ddagger o} + p\Delta V^{\ddagger o} = E_a - RT + p\Delta V^{\ddagger o}$$

where $\Delta V^{\ddagger o}$ is the activation volume. We can subsitute this into the expression for the Transition State Theory rate constant to obtain

$$k_{\mathrm{TST}} = \frac{k_B T}{h} e^{\left(1 + \frac{\Delta S^{\ddagger o}}{R}\right)} e^{-\frac{p\Delta V^{\ddagger o}}{RT}} e^{-\frac{E_a}{RT}}$$

We find that the Arrhenius prefactor becomes

$$A = \frac{k_B T}{h} e^{\left(1 + \frac{\Delta S^{\ddagger o}}{R}\right)} e^{-\frac{p\Delta V^{\ddagger o}}{RT}}$$

For a reaction in solution the activation volume will be approximately zero, $\Delta V^{\ddagger o} = 0$. This is also the case for a unimolecular gas phase reaction. In this case, the expression simplifies to

$$k_{\mathrm{TST}} = \frac{k_B T}{h} e^{\left(1 + \frac{\Delta S^{\ddagger o}}{R}\right)} e^{-\frac{E_a}{RT}}$$

and we can identify the Arrhenius prefactor A with

$$A = \frac{k_B T}{h} e^{\left(1 + \frac{\Delta S^{\ddagger o}}{R}\right)}$$

If instead, we are for example dealing with a gas phase reaction other than a unimolecular reaction, then for ideal gases,

$$p\Delta V^{\ddagger o} = \Delta n^{\ddagger} RT$$

where $\Delta n^{\ddagger}$ is the change of the particle number in the transition state, *e.g.* $\Delta n^{\ddagger} = -1$ for a bimolecular reaction. In this case, we find

$$k_{\mathrm{TST}} = \frac{k_B T}{h} e^{\left(1-\Delta n^{\ddagger}+\frac{\Delta S^{\ddagger o}}{R}\right)} e^{-\frac{E_a}{RT}}$$

so that we can identify the Arrhenius factor with

$$A = \frac{k_B T}{h} e^{\left(1-\Delta n^{\ddagger}+\frac{\Delta S^{\ddagger o}}{R}\right)}$$

APPENDIX A – THE GAMMA FUNCTION

In the context of the kinetic theory of gases and unimolecular reaction dynamics, we frequently encounter integrals of the type $\int_0^\infty x^z e^{-x} dx$ and $\int_0^\infty x^n e^{-ax^2} dx$, which we can solve by means of the gamma function.

$$\boldsymbol{\Gamma(z+1) = \int_0^\infty x^z e^{-x} dx}$$

For any real z, integration by parts gives

$$\int_0^\infty x^z e^{-x} dx = \int_0^\infty -x^z e^{-x} + z x^{z-1} e^{-x} dx = z \int_0^\infty x^{z-1} e^{-x} dx$$

or

$$\Gamma(z+1) = z\Gamma(z)$$

In the special case of z being a positive integer, we find

$$\boldsymbol{\Gamma(n+1) = n!}$$

Moreover, useful relationships are

$$\Gamma(1) = 1$$

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

The gamma function also allows us to solve gaussian integrals of the type $\int_0^\infty x^n e^{-ax^2} dx$. We substitute $ax^2 = y$, so that $x = \left(\frac{y}{a}\right)^{\frac{1}{2}}$ and $dx = \frac{1}{2}(ay)^{-\frac{1}{2}} dy$ and

$$\int_0^\infty x^n e^{-ax^2} dx = \frac{1}{2} a^{-\frac{n+1}{2}} \int_0^\infty y^{\frac{n-1}{2}} e^{-y} dx = \frac{1}{2} a^{-\frac{n+1}{2}} \Gamma\left(\frac{n+1}{2}\right)$$

APPENDIX B –
THE TRANSLATIONAL, ROTATIONAL, AND VIBRATIONAL PARTITION FUNCTIONS

Here we derive expressions for the translational, rotation, and vibrational partition functions.

Translational partition function:

The eigenstates of the particle in a one-dimensional box have energies $\epsilon_n = \frac{h^2}{8ma^2}n^2$, with the quantum number $n = 1, 2, \ldots$ and the length of the box a.

For the corresponding partition function, we obtain

$$q_{trans,1\mathrm{D}} = \sum_n e^{-\frac{\epsilon_n}{k_B T}} \approx \int_0^\infty e^{-\frac{\epsilon_n}{k_B T}} dn = \int_0^\infty e^{-\frac{h^2 n^2}{8ma^2 k_B T}} dn = \frac{a}{h}\sqrt{2\pi m k_B T}$$

The energy of a particle in a three-dimensional box is the sum of three energies for each dimension

$$\epsilon = \epsilon_{n_x} + \epsilon_{n_y} + \epsilon_{n_z}$$

Therefore, the translational partition function for motion in three dimensions is simply the product of three one-dimensional partition functions

$$q_{trans} = q_{trans,1\mathrm{D}}^3 = \left(\frac{a}{h}\sqrt{2\pi m k_B T}\right)^3 = \frac{V}{h^3}(2\pi m k_B T)^{\frac{3}{2}}$$

Rotational partition function:

The eigenstates of the rigid rotor have energies $\epsilon_J = \frac{\hbar^2}{2I}J(J+1) = hcB\,J(J+1)$, with the rotational quantum number $J = 0, 1, 2, \ldots$, the moment of inertia $I = \sum_i m_i r_i^2$, and the rotational constant B. The degeneracy of the levels is $g_J = 2J + 1$.

$$q_{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{hcBJ(J+1)}{k_B T}}$$

For $hcB \ll k_B T$, we can approximate

$$q_{rot} \approx \int_0^\infty (2J+1) e^{-\frac{hcBJ(J+1)}{k_B T}} dJ = \frac{k_B T}{hcB}$$

For symmetric molecules, we have to divide the rotational partition function q_{rot} by the symmetry number σ.

$$q_{rot} = \frac{1}{\sigma}\frac{k_B T}{hcB}$$

The symmetry number is equal to the number of ways to bring the molecule into an equivalent configuration through proper rotations. This is essentially the number of proper rotation operations (including the identity E) of the point group of the molecule. For linear molecules of point group $D_{\infty h}$ such as CO_2, $\sigma = 2$.

Further examples. HCl, $\sigma = 1$; NH_3, $\sigma = 3$; CH_4, $\sigma = 12$.

Vibrational partition function:

The eigenstates of the harmonic oscillator have energies $\epsilon_v = \left(v + \frac{1}{2}\right)\hbar\omega$ with the vibrational quantum number $v = 0, 1, \ldots$ and $\omega = \sqrt{\frac{k}{\mu}}$, where the k is the spring constant, and μ the reduced mass of the oscillator.

$$q_{vib} = \sum_{v=0}^{\infty} e^{-\frac{\left(v+\frac{1}{2}\right)\hbar\omega}{k_B T}} = \sum_{v=0}^{\infty} e^{-\left(v+\frac{1}{2}\right)x}$$

where $x = \frac{\hbar\omega}{k_B T}$ We simplify this expression as follows.

$$q_{vib} e^{-x} = \sum_{v=0}^{\infty} e^{-\left(v+\frac{3}{2}\right)x}$$

$$q_{vib} - q_{vib} e^{-x} = q_{vib}\left(1 - e^{-x}\right) = e^{-\frac{x}{2}}$$

We isolate q_{vib} and finally obtain

$$q_{vib} = \frac{e^{-\frac{x}{2}}}{1 - e^{-x}} = \frac{e^{-\frac{\hbar\omega}{2k_B T}}}{1 - e^{-\frac{\hbar\omega}{k_B T}}}$$