

Reaction Kinetics: Elementary Ideas

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Introduction

Chemical equilibrium deals with chemical systems at *equilibrium*: that is, concentrations (and thus amounts) of chemical species do not change with time.

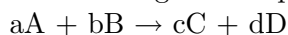
Chemical reaction kinetics attempts to describe the way a non-equilibrium system changes with time in order to achieve chemical equilibrium (of course, with this is tied thermal, mechanical equilibrium)

To reiterate:

1. thermodynamics tells us whether the free energy is associated with a chemical transformation dictates whether the transformation occurs.
2. kinetics tells us how fast (what is the rate) of that transformation towards an equilibrium state. (what is the concentration of a specie(s) as a function of time)

I. Reaction Rates

Consider a generic representation of a chemical reaction:



The *Rate of Reaction* is defined as:

$$Rate = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \quad (1)$$

Experimentally, the Rate of reaction is treated as follows, thus introducing the concept of the *rate constant*, k :

$$Rate = k \prod_{i=1}^N [i]^{\gamma_i} \quad (2)$$

definition of variables:

k = rate constant (sometimes called rate coefficient; can be determined experimentally; can be estimated theoretically—transition state theory)

$[i]$ = concentration of REACTANT species "i"

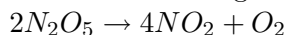
γ_i = Reaction order of REACTANT species "i"

$p = \sum_i \gamma_i$ = overall reaction order

NOTE: at this point, the experimental rate equation is written with species reaction orders that have NO inherent relation to the stoichiometric coefficients (a,b,c,d) of the chemical reaction of interest!

1 Elementary Reactions

Consider the following overall reaction:



The predicted rate law for this reaction (which happens to be in good agreement with experiment) is:

$$rate = \frac{k_1 k_2}{k_{-1} + 2k_2} [N_2O_5] = k_{effective} [N_2O_5] \quad (3)$$

We observe that the overall rate is **NOT** second order in $[N_2O_5]$ as one might quickly jump to conclude. This is because the **mechanism** underlying this overall chemical transformation is **complex**; that is, there are several mechanistic steps involved, with certain intermediates involved as well. We will say more about *reaction mechanisms* later. For the present, we mention them in order to emphasize that the stoichiometric coefficients of the chemical reaction are tied to the reaction order **only for elementary reactions or reaction steps**.

2 Integrated Rate Equations and Analysis for Elementary Reactions

I. Zero'th Order Reactions (rare)

The rate of reaction is independent of instantaneous reactant concentration:



$$Rate = k = -\frac{d[A]}{dt} \quad (4)$$

$$[A]_t = [A]_o - kt \quad (5)$$

The rate constant, k , has units of (concentration/time). The reaction half-life, $t_{1/2}$, is the time necessary for one-half of the reactant species to be consumed is given by:

$$t_{1/2} = \frac{[A]_o}{2k} \quad (6)$$

The units of the rate constant k are in concentration per unit of time ([moles/liter]/sec).

II. First-Order Reactions

A \rightarrow products

The reaction rate for a First-Order reaction is proportional to the *first power* of the concentration of the reacting species (order=1).

$$\text{Rate} = k[A]^1 = -\frac{d[A]}{dt} \quad (7)$$

Integrating this straightforwardly, keeping in mind the *initial concentration of A*, $[A]_o$ is defined (boundary condition for solving differential equation):

$$[A]_t = [A]_o e^{-kt} \quad (8)$$

In order to determine if a reaction is First order, using experimental data, we can manipulate the exponential form just determined into a linear form to make analysis easier.

Taking the natural logarithm (natural log) of both sides to arrive at:

$$\ln [A]_t = \ln [A]_o - kt \quad (9)$$

The half-life of such a reaction is given by:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \quad (10)$$

Using the last relationship, one can reciprocally determine the rate constant knowing the half-life of a reaction or other physicochemical process.

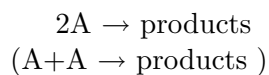
Examples:

- 1. decay of radioactive nuclei (carbon dating)
- 2. fluorescence decay of *electronically* excited molecules
- 3. chemical reactions (as we'll see later)
- 4. others

III. Second Order Reactions

The rate of a second-order reaction is overall 2, and depends on either a single reactant species (to order 2) or on two different reactant species, each with order 1 dependence (recall the definition of reaction order as the sum of the individual species reaction orders). Let's consider the two cases individually.

a). Second order in one reactant



$$\text{Rate} = k[A]^2 = -\frac{1}{2} \frac{d[A]}{dt} \quad (11)$$

Performing the integration:

$$\frac{1}{[A]} = \frac{1}{[A]_o} + 2kt \quad (12)$$

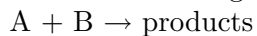
Be careful of the factor of $\frac{1}{2}$ often easily overlooked in the treatment of this reaction.

The half-life for this reaction is given by:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_o} \quad (13)$$

Second order reaction in two reactant species

If the reaction is given by:



the reaction rate is given by:

$$\text{Rate} = k [A]^1 [B]^1 = -\frac{d[A]}{dt} \quad (14)$$

We obtain for the integrated rate equation:

$$kt = \frac{1}{([A]_o - [B]_o)} \ln \frac{[A][B]_o}{[A]_o[B]} \quad [A]_o \neq [B]_o \quad (15)$$

We can now consider two special cases:

- $[A]_o = [B]_o$

- Because of the one-to-one stoichiometry, we can say for all time $[A]=[B]$
- The integrated rate law is like that for 2^{nd} order in one component (see above)
- $[B]_o \lll [A]_o$: we can consider reactant A in excess (it essentially remains **constant**)

$$[B] = [B]_o e^{-k't} \quad (16)$$

- $k' = k[A]_o$
- This is pseudo-1st order (species B undergoing transformation in a "sea of A")

3 Determining Reaction Orders

In order to determine reaction orders, we can play some games with initial concentrations, excesses of species, etc. In order to do this, we need to measure concentrations (or amounts) as a function of time.

- Quench the reaction, measure concentrations
- For gases, measure pressure versus time
- Spectroscopically follow reactant/product species

3.1 Analyzing data

3.1.1 Reactions with 1 reactant

A \rightarrow products

- a. Plot or analyze the time behavior of the concentration;

A vs. time

- $\ln[A]$ vs. time
- $1/[A]$ vs. time
- plot to see which dependence give "straight" line

- b. Half-life method: measure the relation between $t_{\frac{1}{2}}$ and $[A]_o$

- 1st order $\rightarrow t_{\frac{1}{2}} \propto [A]_o^0$
- 2nd order $\rightarrow t_{\frac{1}{2}} \propto [A]_o^{-1}$

c. Multiple Life-times ($t_{\frac{3}{4}}$ and $t_{\frac{1}{2}}$) (at $t_{\frac{3}{4}}, [A] = 0.25[A]_o$)

- 1st order $\rightarrow t_{\frac{3}{4}} = \frac{2\ln 2}{k} \rightarrow \frac{t_{\frac{3}{4}}}{t_{\frac{1}{2}}} = 2$
- 2nd order $\rightarrow t_{\frac{3}{4}} = \frac{3}{[A]_o k} \rightarrow \frac{t_{\frac{3}{4}}}{t_{\frac{1}{2}}} = 3$

3.1.2 Reactions with more than 1 reactant

$A + B + C \rightarrow \text{products}$

a. Initial Rate Method (vary initial concentrations of a species and measure initial rates)

- For $[A]_o \frac{\Delta[A]}{\Delta t}|_{t=0} = R_o \equiv k[A]_o^\alpha [B]_o^\beta [C]_o^\gamma$
- For $[A]'_o \frac{\Delta[A]'}{\Delta t}|_{t=0} = R'_o \equiv k[A]'_o^\alpha [B]_o^\beta [C]_o^\gamma$
- Experimentally determine: $\frac{R_o}{R'_o} = \left(\frac{[A]_o}{[A]'_o}\right)^\alpha$
- Consider the following cases for the scenario: $[A]'_o = 0.5[A]_o$
 - if $\frac{R_o}{R'_o} = 1 \rightarrow \alpha = 0$
 - if $\frac{R_o}{R'_o} = \sqrt{2} \rightarrow \alpha = \frac{1}{2}$
 - if $\frac{R_o}{R'_o} = 2 \rightarrow \alpha = 1$
 - if $\frac{R_o}{R'_o} = 4 \rightarrow \alpha = 2$

b. Flooding or Isolation

- Let $[A]_o \ll [B]_o, [C]_o$ (flood system with B and C)
- Then $[B] \equiv [B]_o$ and $[C] \equiv [C]_o$
- Thus

$$-\frac{d[A]}{dt} \equiv k'[A]^\alpha \quad (17)$$

- $k' = k[B]_o^\beta [C]_o^\gamma$
- the reaction is made to be pseudo- α order with one reactant