Rate Laws

CHEM 361A: Introduction to Physical Chemistry

Dr. Michael Groves

Department of Chemistry and Biochemistry
California State University, Fullerton

Lecture 15

Table of contents

Learning Objective: Define basic rate law equations and derive integrated rate law expressions.

References:

- Atkins and de Paula Focus 6A - 6C
- Chang §12.1 and §12.2

Spontaneity versus speed

Thermodynamics

- Tells us if a process is spontaneous
- State function nature of thermodynamic quantities allows for a big picture type analysis where only the starting reactants and final products are necessary.
- Does not tell us how long it will take to reach equilibrium

Kinetics

- Tells us how fast a process occurs
- A given reaction might involve multiple steps. Proper kinetic analysis requires understanding individual reaction mechanisms to gain an overall grasp of a chemical reaction
- Can tell us equilibrium constants as well as how long it takes to get to equilibrium

Reaction Rates

Consider the following reaction:

$$\mathrm{aA} + \mathrm{bB} \longrightarrow \mathrm{cC} + \mathrm{dD}$$

The number of moles of species i will vary by

$$n_i = n_{i_0} + \nu_i \zeta$$

where

- n_{i_0} is the initial number of moles for species i
- ν_i is the stoichiometric coefficient of species i
- ζ is the advancement of the reaction
- n_i is the amount of species i present given the advancement of the reaction

Reaction Rates (cont.)

Consider the following reaction:

$$\mathrm{aA + bB \longrightarrow cC + dD}$$

The number of moles of species i will decrease by

$$n_i = n_{i_0} + \nu_i \zeta$$

If we were to take the derivative of n_i with respect to time then:

$$\frac{dn_i}{dt} = \nu_i \frac{d\zeta}{dt}$$

If we then rearrange

$$rate = \frac{d\zeta}{dt} = \frac{1}{\nu_i}\frac{dn_i}{dt}$$

Reaction Rate of All Four Species

Still considering the following generalised reaction:

$$\mathrm{aA + bB \longrightarrow cC + dD}$$

write the rate in terms of all four species.

$$rate = -\frac{1}{a}\frac{dn_A}{dt} = -\frac{1}{b}\frac{dn_B}{dt} = \frac{1}{c}\frac{dn_C}{dt} = \frac{1}{d}\frac{dn_D}{dt}$$

Now instead of writing them in terms of moles, write them in terms of concentration

$$\frac{Rate}{V} = \frac{1}{V\nu_i}\frac{dn_i}{dt} = \frac{1}{\nu_i}\frac{d[i]}{dt}$$

Reaction Order

Still considering the following generalised reaction:

$$\mathrm{aA} + \mathrm{bB} \xrightarrow{k_f} \mathrm{cC} + \mathrm{dD}$$

The rate can also be determined empirically

$$rate = -\frac{1}{a}\frac{d[A]}{dt} = k_f[A]^x[B]^y$$

where k_f is the **rate constant** for the forward reaction. Note

- The **order** of each component is the power it is raised to (fx. x and y)
- The overall order of the reaction is the sum of all powers $(x + y)$
- The **orders** are **not** related to the **stoichiometric coefficients** in the overall balanced reaction

Examples in Reaction Order

For the following rate laws, write down the order of each component and the total order:

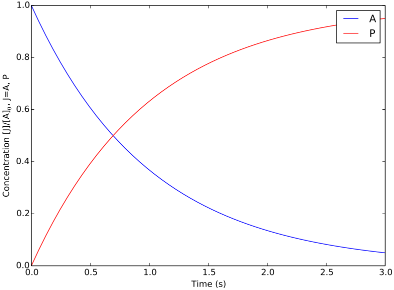
1. $$rate = [A]^2[B]$$
2. $$rate = [A]^{\frac{1}{2}}[B]^3$$
3. $$rate = \frac{k_r[E][S]}{[S] + K_M}$$

Integrated Rate Law Expressions

Given a reaction

$$A \xrightarrow{k_f} P$$

If we know the order of a reaction and the initial conditions, we can integrate rate law expressions, and predict the concentration of reagents at any time.



$$\frac{d[A]}{dt} = -k_f[A]^x \quad \rightarrow \quad \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^x} = \int_0^t -k_f \; dt$$

Zero-Order Reactions

Consider the reaction

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

If the rate is given by:

$$rate = -\frac{d[A]}{dt} = k_f[A]^0 = k_f$$

Then the rate is independent of $[A]$ and can be found at any time, t, using:

$$[A] = [A]_0 - k_f t$$

First Order Reactions

Again consider the reaction

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

If the rate is given by:

$$rate = -\frac{d[A]}{dt} = k_f[A]$$

Then the rate is dependent on $[A]$ and $[A]$ can be found at any time, t, using:

$$\ln[A] = \ln[A]_0 - k_f t$$

Second Order Reactions (type 1)

Again consider the reaction

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

If the rate is given by:

$$rate = -\frac{d[A]}{dt} = k_f[A]^2$$

then the rate is dependent on $[A]$ and $[A]$ can be found at any time, t, using:

$$\frac{1}{[A]} = \frac{1}{[A_0]} + k_f t$$

Second Order Reactions (type 2)

Again consider the reaction

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

If the rate is given by:

$$rate = -\frac{d[A]}{dt} = k_f[A][B]$$

then the rate is dependent on both $[A]$ and $[B]$ where the concentration of both can be found at any time, t, using:

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

A Note on Simplifying Complicated Rate Laws

Consider the reaction

$$\mathrm{CH_3COCl(aq) + H_2O(l) \xrightarrow{k_f} CH_3COOH(aq) + HCl(aq)}$$

The rate is governed by the second order expression:

$$rate = -\frac{d[\mathrm{CH_3COCl}]}{dt} = k_f[\mathrm{CH_3COCl}][\mathrm{H_2O}]$$

However, H_2O is in large excess so its concentration will not change as the reaction progresses. Therefore

$$rate = -\frac{d[\mathrm{CH_3COCl}]}{dt} = k_f'[\mathrm{CH_3COCl}]; \quad \text{where } k_f' = k_f[\mathrm{H_2O}]$$

Now we can solve this as a first order reaction.

Strategies to Find Orders

We can use empirical data as well as rate law and integrated rate law expressions to determine the order of components

1. Isolation Method - Keep all the [reactant's] constant except one which simplifies the rate law to a single component
2. Integration Method - Measure the concentration of the components at various times and evaluate the data with each rate law. Not very accurate.
3. Differential Method - Starting with the rate law, take the logarithm to both sides and solve for the orders
4. Half-life Method - Measuring how long it takes for half the concentration to remain is dependent on the order of the reaction.

Example of the Differential Method

Consider the following reaction:

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

determine the order of the reaction with respect to A and B, as well as the rate constant for the reaction:

[A] (M)	[B] (M)	Initial Rate ($\mathrm{M\ s^{-1}}$)
2.30×10^{-4}	3.10×10^{-5}	5.25×10^{-4}
4.60×10^{-4}	6.20×10^{-5}	4.20×10^{-3}
9.20×10^{-4}	6.20×10^{-5}	1.68×10^{-2}

Example of the Half-Life Method

The half-life of certain orders of reactions are:

Order	Expression
0	$t_{1/2} = [A]_0/2k$
1	$t_{1/2} = \ln 2/k$
2 (type 1)	$t_{1/2} = 1/k[A]_0$

For the reaction

$$\mathrm{A} \longrightarrow \mathrm{B}$$

when the concentration of A was change from 1.20 M to 0.6 M, the half-life increased from 2.0 mins to 4.0 mins at 25°C. Calculate the order of the reaction and the rate constant.

Summary

- Rate laws are empirical expressions used to describe how components in a reaction change with time
- When integrated, the integrated rate law expressions can be used to predict the concentration of each component at a given time.
- These expressions can be used to determine the order of a reagent, which quantifies how influential a given component is to the overall reaction.
- The order also determines the component's half-life, the time it takes for half of the original amount to be left.