

CHEM 116

Why Different Reactions Have Different Rate Laws

October 12, 2006
Prof. Sevian



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Agenda

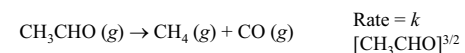
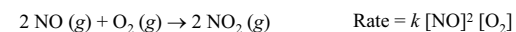
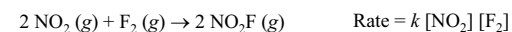
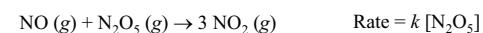
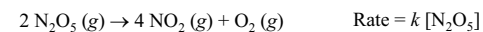
Kinetics: the study of how fast reactions occur

- What factors affect reaction rates?
- How do we measure reaction rates? How do reaction rates differ from one another?
 - Measure concentration vs. time and examine graph
 - Vary concentrations of one or another reactant
 - Finding order of reaction rate with respect to various reactants
 - Determining rate constant
- Using experimentally determined rate laws to predict concentrations after some amount of time
 - Half life
- A closer inspection of rate constants (k in the rate law)

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Rate law must be determined experimentally

Some reactions and their *experimentally determined* rate laws



Important: Order of rate determined by experiment may not match stoichiometric coefficients

Key points about kinetics so far

- Study the vocabulary
- Reaction rate has weird units
- Be clear whether you are talking about average reaction rate or instantaneous reaction rate
- The equations which we will study all talk about instantaneous reaction rate, most easily measured at the beginning of a reaction (initial rate)
- Relating rates at which products appear (+) and reactants disappear (-) has to do with inverse stoichiometric coefficients
- Reaction rate depends on several factors: initial concentration, temperature, surface area of reactants exposed, presence of a catalyst

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Order of reaction rate

- Rate of reaction can depend on how much reactant is present in more than one way

Zero order:
rate $\propto [A]^0$

First order:
rate $\propto [A]$

Second order:
rate $\propto [A]^2$



What does "order" mean?

- Zero order
rate = $k[A]^0$
if you double [A] rate stays the same
[A] $\times 2$ rate $\times 2^0 =$ stays same
if you triple A, [A] $\times 3$ rate $\times 3^0 =$ stays same
- First order
rate = $k[A]^1$
if you double [A] rate doubles
[A] $\times 2$ rate $\times 2^1$
if you triple A, [A] $\times 3$ rate $\times 3^1$
- Second order
rate = $k[A]^2$
if you double [A] rate quadruples
[A] $\times 2$ rate $\times 2^2 =$ rate $\times 4$
if you triple A, [A] $\times 3$ rate $\times 3^2 =$ rate $\times 9$

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Two ways to figure out the dependence of the rate on concentration of chemicals in the reaction

- Graph concentration vs. time and examine mathematical shape of curve

- Zero order

$$\text{rate} = k[A]^0$$

$$-\frac{d[A]}{dt} = k \rightarrow \int_{\text{when } t=0}^{\text{at time } t} d[A] = -\int k dt \rightarrow [A]_t = [A]_0 - k t$$

$$y = a + bx$$

- First order

$$\text{rate} = k[A]^1$$

$$-\frac{d[A]}{dt} = k[A] \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]} = -\int k dt \rightarrow \ln[A]_t = \ln[A]_0 - k t$$

$$y = a + bx$$

- Second order

$$\text{rate} = k[A]^2$$

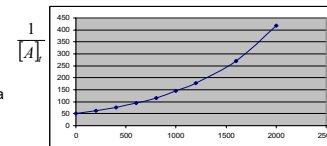
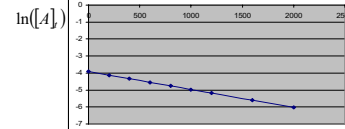
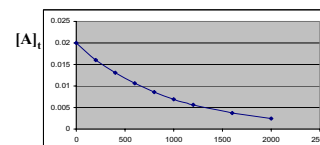
$$-\frac{d[A]}{dt} = k[A]^2 \rightarrow \int_{\text{when } t=0}^{\text{at time } t} \frac{d[A]}{[A]^2} = -\int k dt \rightarrow \frac{1}{[A]_t} = \frac{1}{[A]_0} + k t$$

$$y = a + bx$$

- Measure initial rate at many different initial concentrations and compare

Method 1: Comparing graphs

Time (min)	[H ₂ O ₂] (M)
0	0.0200
200	0.0160
400	0.0131
600	0.0106
800	0.0086
1000	0.0069
1200	0.0056
1600	0.0037
2000	0.0024



Key question is: which one is a straight line?

Method 2: Determining rate law by measuring initial rate at various concentrations

Example

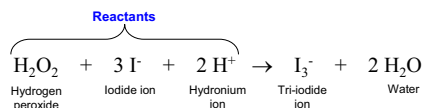
Given the following measurements of initial rate of reaction under various conditions of initial concentrations of reactants, determine:

- the rate law
- the value of the rate law constant, k
- the units of k

Experiment	Initial Concentration (M)		Initial rate (M/s)
	[NO]	[O ₂]	
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

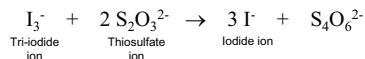
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Iodine clock reaction

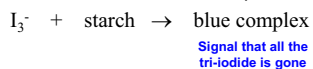


And then, two things can happen:

- Tri-iodide gets reduced back to iodide ion by thiosulfate



- When the thiosulfate gets used up, tri-iodide reacts with starch to form blue starch-triiodide complex



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What experiments can be done?

- Vary H⁺ concentration
- Vary I⁻ concentration
- Vary H₂O₂ concentration
- Change temperature

Half-life

The amount of time it takes for half of the reactant to react (disappear)

Mathematical definition

Need to find time at which concentration of the reactant is equal to half the initial concentration

[A] is a function of t

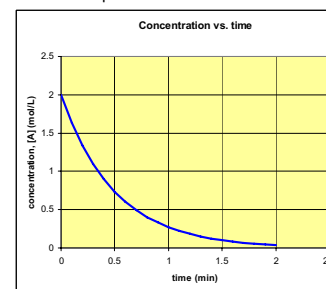
For first - order, [A]_t given by

$$\ln[A]_t = \ln[A]_0 - kt$$

Half - life is the value of t when

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

Graphical definition



General equation for half-life

If the reaction is first-order, meaning $\left\{ \begin{array}{l} \text{Rate} = \frac{\Delta[A]}{\Delta t} = k[A] \\ \ln[A] = \ln[A]_0 - kt \end{array} \right.$ differential rate law
integrated rate law

and if you know the value of the rate law constant k , then you can determine the half-life algebraically

Looking for value of t when $[A] = \frac{1}{2}[A]_0$, or $\frac{[A]}{[A]_0} = \frac{1}{2}$

$$\ln[A] = \ln[A]_0 - kt$$

Rearranging,

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

So at the time where half the reactant is gone:

$$\ln(2) = k t_{\text{half-life}}$$

$$t_{\text{half-life}} = \frac{\ln(2)}{k}$$

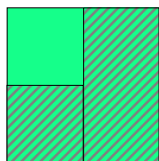
$$t_{\text{half-life}} = \frac{0.693}{k}$$

or

$$k = \frac{t_{\text{half-life}}}{0.693}$$

Sometimes it is easier to work with the half-life

Example: If a given reaction is first-order and the half-life is 2.5 minutes, how much reactant remains after 5.0 minutes have passed if the initial amount of reactant is 100. grams?



Amount of reactant	# of half-lives
All (100%)	0
Half (50%)	1
One-fourth (25%)	2
One-eighth (12.5%)	3

Amount of reactant remaining:

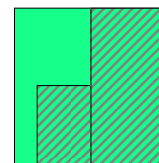
$$[A] = \left(\frac{1}{2}\right)^{\text{\# of half-lives}} [A]_0$$

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Sometimes it is easier to work with the half-life

Example: If a given reaction is first-order and the half-life is 2.5 minutes, how much reactant remains after 4.0 minutes have passed if the initial amount of reactant is 100. grams?

Amount of reactant	# of half-lives
All (100%)	0
Half (50%)	1
One-fourth (25%)	2



$$[A] = \left(\frac{1}{2}\right)^{\text{\# of half-lives}} [A]_0$$

$$\text{\# of half-lives} = \frac{\text{time}}{t_{\text{half-life}}} = \frac{4.0 \text{ min}}{2.5 \text{ min}} = 1.6$$

$$[A] = \left(\frac{1}{2}\right)^{1.6} [A]_0 = 0.3299(100.\text{g}) = 33 \text{ g}$$

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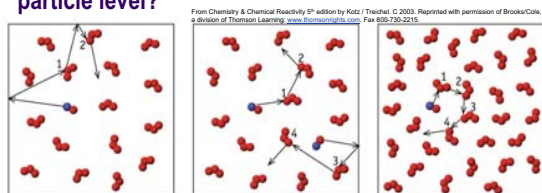
All nuclear decay processes are first-order

Example

Radioactive iodine-125, which is used for studies of thyroid functioning, has a rate constant for decay of 0.011 day^{-1} . If you begin a treatment with iodine-125, and start with 1.6×10^{15} atoms, how many atoms remain after 2.0 days?

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Reaction rates: what's happening at the particle level?



(a) 1 NO: 16 O₃ - 2 hits/second (b) 2 NO: 16 O₃ - 4 hits/second (c) 1 NO: 32 O₃ - 4 hits/second

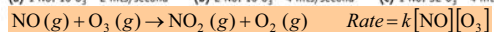
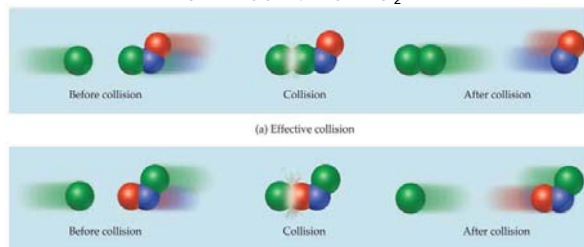
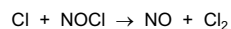


Figure	Ratio of NO:O ₃	# of collisions per sec
(a)	1/16	2
(b)	2/16	4
(c)	1/32	4

For a nice review of these concepts, along with animations, see <http://www.sciencepages.co.uk/keystage4/GCSEChemistry/m3ratesofreaction.php>

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Why isn't collision frequency the only factor affecting reaction rate?



(a) Effective collision
(b) Ineffective collision
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Why is (a) effective and (b) is ineffective?

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What affects the reaction rate?

Macroscopic level

Evidence: use experimental measurements to determine orders and value of k in rate law

- When you increase reactant concentrations, rate of reaction increases
- When you increase temperature, rate of reaction increases
- Some reactions have very slow rates and some very fast rates - what differs is the value of k

Particle level

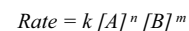
What we *believe* is happening at the particle level that explains why reaction rates have the mathematical form they do

- When there are more reactant particles, they collide more often
- When the average speeds of reactant particles increases, they collide more often
- There must be some reason for this at the particle level...

Assumption: Rate laws always have the mathematical form
 $\text{Rate} = k [\text{A}]^n [\text{B}]^m$

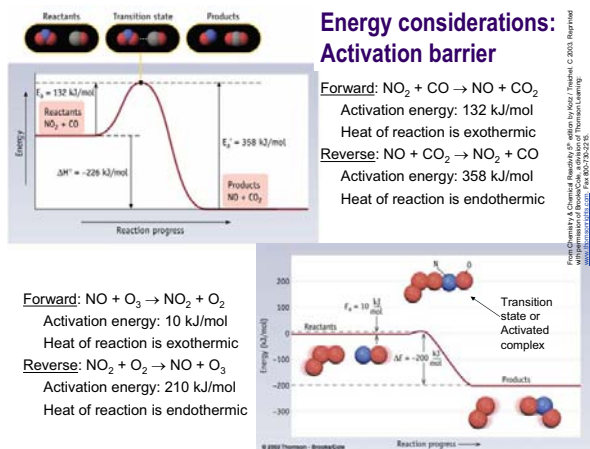
Assumption: in order for molecules to react with each other, they must collide

What is the theoretical basis for the form of the rate law? Must be based on how particles behave.



- Numbers of particles: reflected in concentration
- Temperature: must be part of k
- There must be something else that is part of k that explains why two reactions at the same T can have different values of k

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What does the rate constant depend on?

$$k = A e^{-\frac{E_a}{RT}}$$

Rate constant that appears in the rate law:
 $\text{Rate} = k [\text{A}]^m [\text{B}]^n$

(Note - unfortunate coincidence: same letter A used for this constant and generic reactant name.)

A constant that depends on the fraction of collisions in which molecules collide with an orientation that a reaction will result from

Temperature (in Kelvin): as temperature gets higher, k gets larger

Activation energy barrier: as E_a gets larger, k gets smaller

Experimental determination of activation energy

$$k = A e^{-\frac{E_a}{RT}}$$

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

$$(\ln k) = (\ln A) - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

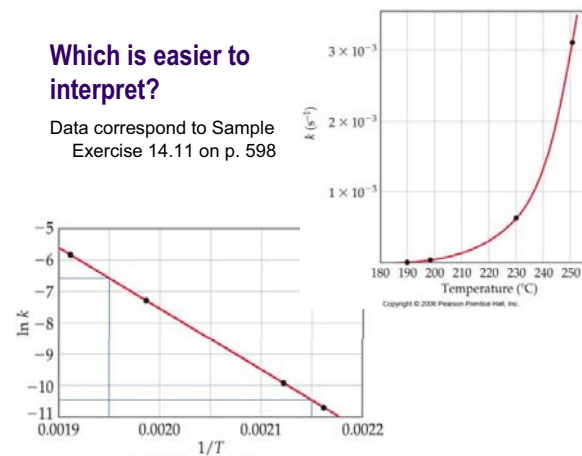
$$y = a + b x$$

Experimental scenario:

1. Determine form of rate law
2. Form should remain the same at different temperatures
3. Run experiments at many temperatures and experimentally determine k vs. T

Which is easier to interpret?

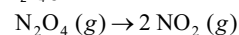
Data correspond to Sample Exercise 14.11 on p. 598



Calculating activation energy from rate constant vs. temperature data

Example

The decomposition of N_2O_4 gas is first order.



The rate constant $k = 4.5 \times 10^3 \text{ s}^{-1}$ at $1.0 \text{ }^\circ\text{C}$ and $1.00 \times 10^4 \text{ s}^{-1}$ at $10.0 \text{ }^\circ\text{C}$. What is the activation energy?

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Key points about kinetics from today

- There are two ways to determine a rate law experimentally
 1. Data needed: concentration vs. time as a single experiment progresses
Process: graph versions of $[A]$ vs. versions of t to determine value of n in $d[A]/dt = -k[A]^n$
 2. Data needed: multiple experiments varying initial concentration, measure initial rate for a chemical in the rxn
Process: compare experiments to determine values of n (and m) for each reactant in rate = $k[A]^n[B]^m$
- In a first-order reaction, it is often easier to work with half-life to predict amount of reactant remaining
- Rate law constant, k , depends on temperature and activation energy, E_a , as well as other factors (e.g., % of collisions that are properly oriented). Value of E_a can be determined by measuring k vs. T and using Arrhenius equation to interpret results.

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Learning from Exam 1

What the class did well on:

- Single step arguments about intermolecular forces (e.g., the stronger the IM forces, the ___ the boiling point, or in which gas are forces strongest)
- Calculations involving the gas laws
- Density of gases
- Reading phase diagrams and understanding meaning of vapor pressure

What the class didn't do well on:

- Graham's law of effusion
- Recognizing hydrogen bonding
- Moving between words and calculations involving gas laws
- Identifying conditions under which gases behave less ideally
- Determining whether a compound is molecular, ionic or metallic and connecting those with macroscopic properties

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Graham's law of effusion

- Air, being about 16 times as dense as hydrogen, diffuses:

- 16 times as fast
- 4 times as fast
- $1/16$ as fast
- $1/4$ as fast
- $1/2$ as fast

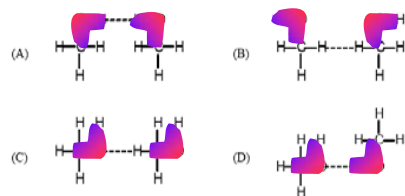
Should air diffuse faster or slower than hydrogen? Why?

$$\frac{v_{air}}{v_{hydrogen}} = \sqrt{\frac{M_{hydrogen}}{M_{air}}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

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Recognizing H bonding

- Which represents hydrogen bonding?



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Words and math

- Air is sealed in a vessel at 273°C and then cooled to 0°C. If the vessel itself does not contract, the pressure inside the vessel will become
 - zero
 - one-fourth of its original value
 - one-half its original value
 - twice its original value
 - none of these

$$T_1 = 273^\circ\text{C} + 273 = 546\text{K}, T_2 = 0^\circ\text{C} = 273\text{K}$$

"does not contract" = volume stays constant

"sealed" = moles (n) stay constant

$P_1 = \text{some value}, P_2 = \text{compare to } P_1$

Direct relation, so if $T \downarrow$ then P also \downarrow by same factor

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Properties of materials and metallic, molecular or ionic compound

- Which substance meets the requirements: solid at room temperature but low melting point, poor electrical conductor?
 - $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 - Ag
 - Na_2SO_4
 - CH_4

Metals

Molecular substances

Ionic substances

A website to help you review this, view 3-d moveable chemical structures, and practice identifying different substances:

<http://www.creative-chemistry.org.uk/molecules/structures.htm> ³¹