

Lecture 19: KINETICS CALCULATIONS USING THE DIFFERENTIAL AND INTERGRATED RATE LAWS

How to do the famous kinetic calculations, applied to 0th, 1st and 2nd order reactions

In this lecture you will learn to do the following

- Determine reaction order from units
- Determine reaction order from method of initial rates
- Calculate “k” from rate equation
- Convert how fast (differential rate equation) into how much (integrated rate equation) using calculus
- Use integrated rate law to find half lives
- Use integrated rate law to find extent of reaction

First we review the differential rate equation and define the pieces of the rate law:

$$\underbrace{\frac{\Delta [R]}{\Delta t}}_{\substack{\text{Rate} \\ \text{From} \\ \text{Slope}}} = \text{rate} = [R]^x \underbrace{A \exp [-E_a/RT]}_{\substack{\text{rate constant, } k}} = \underbrace{k [R]^x}_{\text{rate law}}$$

Note that there are four physical parameters in the rate law that determine the rate of reaction:

1. $[]^x$ concentration and order of reactants and products
 2. E_a activation energy
 3. T temperature
 4. A pre-exponential factor
- } the three factors making up k , the rate constant

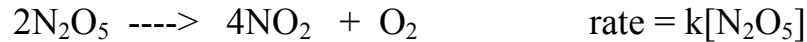
We will save learning to do calculations involving parameters 2-4 for Lecture 3 when we learn about kinetic theory and concentrate for now on the concentration term, $[R]$, and how the order of reaction, x .

$$[R]^x$$

Order of Reaction

In the rate equation: $\text{rate} = k [\text{R}]^x$, x is the order of reaction in the function that describes how concentration affects rate.

Example of reaction order:



This reaction is **first order in $[\text{N}_2\text{O}_5]$** and **first order overall**.

Example of reaction order:



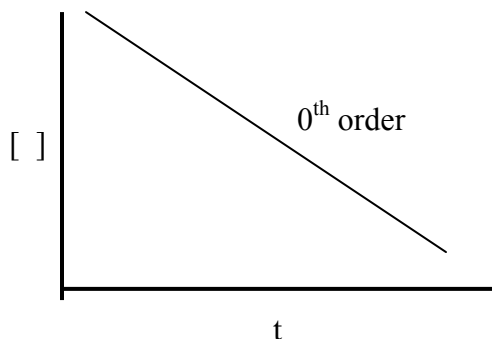
This reaction is **first order in NO** and **in O_2** and **second order overall**.

We will look at three examples of reaction order in this lecture.

order	rate equation	effect of concentration on rate
0	$\text{rate} = k[\text{R}]^0 = k$	none
1	$\text{rate} = k[\text{R}]^1$	rate increases linearly with concentration
2	$\text{rate} = k[\text{R}]^2$	rate increases as the square of the concentration

Example 1: 0th order $x = 0$ so $\text{Rate} = k [\text{R}]^0 = k$

This means that rate is independent of concentration $[\text{R}]$ as is shown below. Note that no matter what the concentration, the slope does not change.

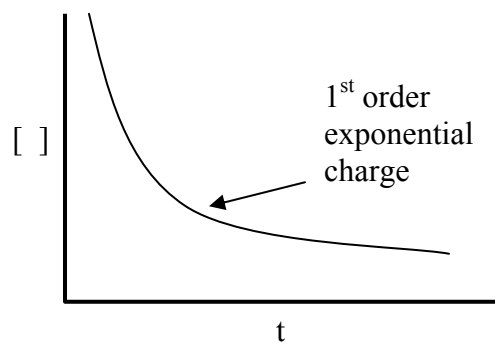


Example 2: 1st order

$x = 1$

$\text{Rate} = k [\text{R}]^1$

This means that rate varies with concentration $[\text{R}]$ and as we saw in class, follows an exponential function—very fast initial rates and then, at longer times, a very small slope.

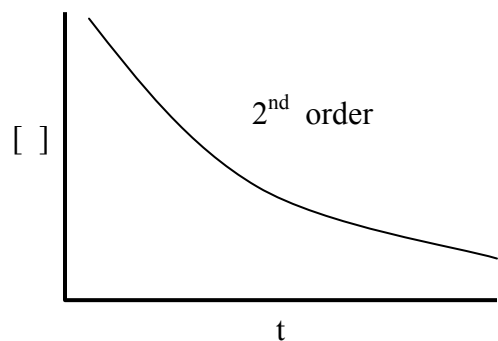


Example 3: 2nd order

$x = 2$

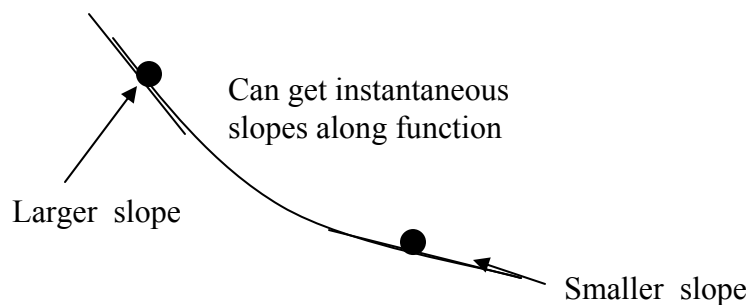
$\text{Rate} = k [\text{R}]^2$

This means that rate varies with concentration $[\text{R}]^2$ and is most commonly associated with bimolecular collision reactions—what you would traditionally think of as the way a reaction happens \rightarrow A collides with B and makes a product. $\text{A+B} \rightarrow \text{P}$. This kind of reaction is actually less likely than you might think, as we will learn when we get to kinetic theory.



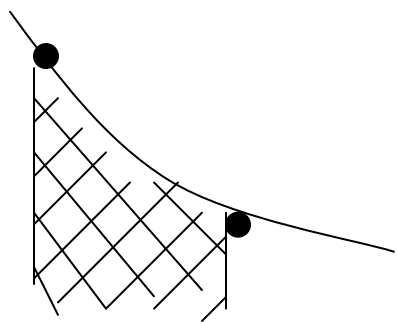
TIME OUT FOR CALCULUS. The rest of this lecture will follow what happens in two equations, a differential rate equation and an integrated rate equation. Just a reminder of what you should have learned in calculus as a scientist, if you learned nothing else:

Differential Calculus Tells how fast something happens—it is a value found from the instantaneous slope of a function.



Integral Calculus

Tells us how much we have of something and is found from area under the curve made by a function.



Understand that how fast (from the differential rate equation) and how much (from the integral rate expression) are really what we most want to calculate in kinetics—and we are using the simple tools we learned in calculus to do it.

Well That is pretty much it for calculus—back to kinetics. Let's look at kinetics calculations for reactions with different reaction order. Look at $x = 0, 1, 2$

First, look at $x = 1 = \text{first order reaction}$ in the simple reaction below



We know that the rate is found from the slope of either R or P

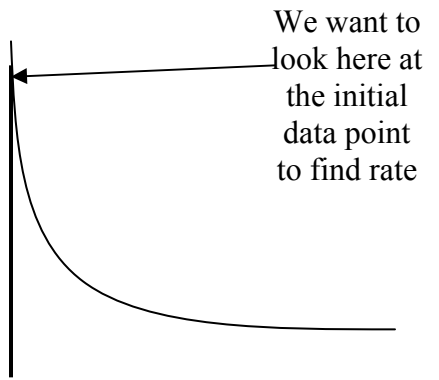
$$\frac{-\Delta [R]}{r\Delta t} = +\frac{\Delta [P]}{p\Delta t} = \text{rate} = k [R]^x [P]^y$$

and the rate law tells us how concentration matters—but how do we find out x and y ?

There are a variety of methods, and in fact I have a nice summary sheet posted on the many ways to find the order of a reaction. But experimentally, in lab you will use something called:

Method of initial rates

Run multiple kinetics experiments with different starting amounts. For each, find the slope (rate) of the reaction right at the start. Note in the data below that we are being intelligent scientists by holding one concentration constant while varying the other. This allows us to isolate how the concentration effects the rate of reaction.



Data for a method of initial rates problem with three experimental rates determined.

	[R]	[P]	rate
Experiment 1	.1M	.1M	2×10^{-4}
Experiment 2	.2M	.1M	4×10^{-4}
Experiment 3	.2M	.2M	4×10^{-4}

First, find order of R (the values of x)

Mathematically this is the ratio of the rate of reaction to the concentration [R] in experiments 1 and 2 where [P] is held constant.

$$\frac{4 \times 10^{-4}}{2 \times 10^{-4}} = \left[\frac{0.2}{0.1} \right]^x$$

And solving:

$$2 = 2^x \quad \text{so } x = 1 \quad \text{and R is first order}$$

Now, what is the order of P (the value of y)?

Do the same way using experiments 2 and 3 in which [R] is held constant.

$$\frac{4 \times 10^{-4}}{4 \times 10^{-4}} = \left[\frac{0.2}{0.1} \right]^y$$

And solving: $1 = 2^y$ so $y = 0$ so P is 0^{th} order

Overall the first order rate law is: $\text{rate} = \frac{\Delta [\underline{R}]}{\Delta t} = k [\underline{R}]^1 [\underline{P}]^0 = k[\underline{R}]^1$

Now can we find value of k? Stick in data from method of initial rates. Use experiment 1.

$$\text{Rate} = 2 \times 10^{-4} = k [0.1]^1 \quad k = 2 \times 10^{-3} = \text{rate constant which is the same for all experiments}$$

Can we also find the units of k?

Simply cancel units in rate expression

$$\frac{[\text{R}]}{t} = k [\text{R}] \quad \text{cancel and } 1/t = k$$

This means that the units for first order rate expression are reciprocal time: like sec^{-1}

$$\text{So } k = 2 \times 10^{-3} \text{ sec}^{-1}$$

Integrated Rate Equation for a first order process.

Recall that earlier I suggested it might be nice to know what the function was that described the relationship between concentration and time for a reaction curve. Here is our chance.

The good news is that the equations we will develop to describe the kinetic reactions fall into a few simple categories which are a function of the order of a reaction. In other words, all zero order reactions have the same shape to the curve; all first order reactions have the same shape to the curve; all second order reactions have the same shape to the curve.

The bad news is that we have to use calculus to find the equation.

Lets do it for just the first order integrated rate equation since it is really famous. This is the one that describes radioactive decay and a million other things.

Can we find the area under a curve and determine how much we have at any time:

Now let's do some calculus to see **how much** occurs in first order reactions. Note that we will be using very simple functions that you have learned to integrate way back in baby calculus.

$$-\frac{\Delta [R]}{\Delta t} = k [R]^1$$

Rearrange $-\frac{\Delta [R]}{[R]} = rk\Delta t$

Integrate $\int -\frac{\Delta [R]}{[R]} = \int rk\Delta t$

Solve $-\ln [R] \bigg|_0^f = rkt \bigg|_0^f$

And solving: $-(\ln [R_f] - \ln [R_0]) = rk (t_f - t_0)$

And rearranging:

$$\ln [R_f] = \ln [R_0] - rkt \quad \leftarrow \text{The answer: How much is left } [R_f] \text{ from what starts } [R_0], \text{ for given } k \text{ and } t \text{ values in a first order process}$$

Applications of Integrated 1st order Equation

1. **Half life equation.** How much time does it take for half of starting amount to go away in a first order reaction?

So $t_{1/2} =$ half life when $R_f = 0.5 R_0$
and substituting:

$$\ln [R_f] = \ln [R_0] - rkt \quad \text{at } t_{1/2}$$

$$\ln [0.5 R_0] = \ln [R_0] - rkt \quad \text{and if for example, } R_0 = 1 \text{ and } R_f = 0.5$$

then: $t_{1/2} = (0.693/rk)$

and rearranging $0.693/rk = t_{1/2}$

WOW!! The half life for a first order reaction is independent of concentration

2. **A garden variety integrated rate law calculation.** How much is stuff is left if we start with $R_0 = 0.1 \text{ M}$ and $k = 2 \times 10^{-3} \text{ sec}^{-1}$ after 100 sec?

$$\ln [R_f] = \ln [0.1] - (1) (2 \times 10^{-3})(100)$$

$$\ln [R_f] = -2.5$$

$$R_f = 0.082 \text{ so } 18\% \text{ has gone away after } 100 \text{ s}$$

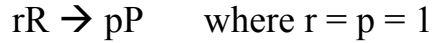
As we finish up first order calculations, note that

$\ln [R_f] = \ln [R_0] - rkt$ is the integrated first order rate law and you will use it a million times when

problem solving to answer the question “**how much**” in kinetics. This equation gives us what we want: for any starting concentration and rate constant, you can stick in a time and it will tell you what the concentration is

Calculations involving zeroth order reactions:

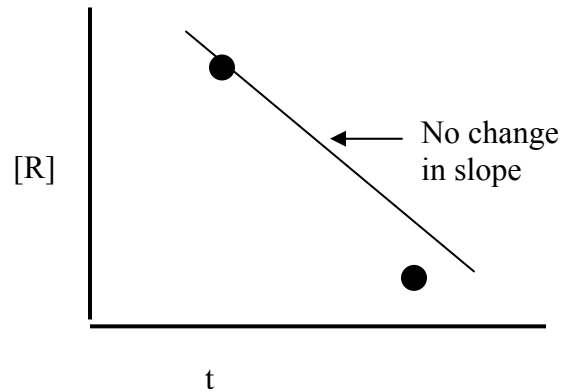
Consider the simple reaction:



For a zeroth order reaction the rate expression is

$$\text{Rate} = \frac{-\Delta[R]}{\Delta t} = k[R]^0[P]^0 = k$$

And a plot of concentration versus time has an invariant slope



First let's look at a method of initial rates calculation that would involve a zeroth order reaction. Note that no matter how the concentrations are varied, the rate is a constant.

Data for method of initial rates calculation

	[R]	[P]	rate
Experiment 1	.1M	.1M	2×10^{-3}
Experiment 2	.2M	.1M	2×10^{-3}
Experiment 3	.2M	.2M	2×10^{-3}

Order of R (Experiments 1 and 2)

Mathematically this is the ratio of the rate of reaction to the concentration [R] in experiments 1 and 2 where [P] is held constant.

$$\left[\frac{2 \times 10^{-3}}{2 \times 10^{-3}} \right] \left[\frac{0.2}{0.1} \right]^x$$

And solving:

$$1 = 2^x \quad \text{so} \quad x = 0$$

Order of P (Experiments 2 and 3)

Mathematically this is the ratio of the rate of reaction to the concentration [P] in experiments 2 and 3 where [P] is held constant.

$$\left[\frac{2 \times 10^{-3}}{2 \times 10^{-3}} \right] \left[\frac{0.2}{0.1} \right]^y$$

And solving:

$$1 = 2^y \quad \text{so} \quad y = 0$$

$$\text{So, Rate} = k[\text{R}]^0[\text{P}]^0 = k$$

What is k here?

Substitute values for rate law from Experiment 1

$$\text{Rate} = 2 \times 10^3 = k[\text{R}]^0[\text{P}]^0$$

$$k = 2 \times 10^3$$

What are the units of the rate constant?

$$\text{Rate} = [\text{]/t} = k$$

So pretty obviously,

$$0^{\text{th}} \text{ order units are } k = [\text{]/t \text{ or } [\text{] t}^{-1} \text{ or Msec}^{-1} \quad \text{and} \quad k = 2 \times 10^3 \text{ Msec}^{-1}$$

Solving for the 0th order integrated rate law.

Integrate 0th order differential rate equation to find out how much stuff reacts over a given time period:

$$-\frac{\Delta[R]}{\Delta t} = k$$

$$\int \Delta[R] = \int rk\Delta t$$

$$-[R] \Big|_0^f = rkt \Big|_0^f$$

$$[R_f] = [R_0] - rkt$$

Applications of Integrated 0th order Equation

1 **Half Life Equation.** How much time does it take for half of starting amount to go away in a first order reaction?

So $t_{1/2}$ = half life when $R_f = 0.5 R_0$

and substituting:

$$\text{So } 0.5 [R_0] = [R_0] - rkt_{1/2}$$

So $t_{1/2} = (0.5R_0/rk)$ Notice in this case the half life is concentration dependent.

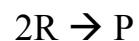
2 **A garden variety integrated rate law calculation.** How much do I have left if $[R_0] = 0.1 \text{ M}$ and $k = 2 \times 10^3 \text{ M/s}$ after 10 microseconds?

$$[R_f] = 0.1 \text{ M} - (1) (2 \times 10^3 \text{ M/s}) (10 \times 10^{-6} \text{ s})$$

$$[R_f] = 0.1 - 0.02 = 0.08 \text{ M} \quad \text{So after 10 microseconds, 20\% is gone}$$

Calculations involving second order reactions:

Consider the simple reaction:



$$\text{Rate} = -\frac{\Delta[R]}{2 \Delta t} = k[R]^x[P]^y$$

What are x and y?

Use method of initial rates. For a second order reaction the rate expression is

$$\text{Rate} = -\frac{\Delta[R]}{\Delta t} = k[R]^2[P]^0 = k$$

First let's look at a method of initial rates calculation that would involve a second order reaction.

Data for method of initial rates calculation

	[R]	[P]	rate
Experiment 1	.1M	.1M	4×10^{-2}
Experiment 2	.2M	.1M	16×10^{-2}
Experiment 3	.2M	.2M	16×10^{-2}

Order of R (Experiments 1 and 2)

Mathematically this is the ratio of the rate of reaction to the concentration [R] in experiments 1 and 2 where [P] is held constant.

$$\left[\frac{16 \times 10^{-2}}{4 \times 10^{-2}} \right] = \left[\frac{0.2}{0.1} \right]^x$$

And solving:

$$4 = 2^x \quad \text{so} \quad x = 2$$

Order of P (Experiments 2 and 3)

Mathematically this is the ratio of the rate of reaction to the concentration [P] in experiments 2 and 3 where [P] is held constant.

$$\left[\frac{16 \times 10^{-2}}{16 \times 10^{-2}} \right] = \left[\frac{0.2}{0.1} \right]^y$$

And solving:

$$1 = 2^y \quad \text{so} \quad y = 0$$

$$\text{So, Rate} = k[\text{R}]^2[\text{P}]^0 = k [\text{R}]^2$$

What is k here?

Substitute values for rate law from Experiment 1

$$\text{Rate} = 4 \times 10^{-2} = k(0.1)^2$$

$$k = 4$$

What are the units of the rate constant?

$$\text{Rate} = \frac{[]}{t} = k []^2$$

So

2nd order units are $[]^{-1} t^{-1}$ or $M^{-1} \text{sec}^{-1}$

and $k = 4 M^{-1} \text{sec}^{-1}$

Solving for the integrated rate law.

Integrate 2nd order differential rate equation to find out how much stuff reacts over a given time period:

$$-\frac{\Delta[R]}{r \Delta t} = k[R]^2$$

$$\int \frac{\Delta[R]}{[R]^2} = \int rk \Delta t$$

$$-(-1/[R]) \Big|_0^f = rkt \Big|_0^f$$

$(1/[R_f]) = (1/[R_0]) + rkt$ ← Second order integrated rate law

Applications of Integrated 2nd order Equation

1 **Half Life Equation.** How much time does it take for half of starting amount to go away in a first order reaction?

So $t_{1/2} = \text{half life when } R_f = 0.5 R_0$
and substituting:

$(1/rk R_0) = t_{1/2}$ Notice in this case the half life is concentration dependent.

2 **A garden variety integrated rate law calculation.** How much do I have left if $[R_0] = 0.1 \text{ M}$ and $k = 4 \text{ s}^{-1} \text{ []}^{-1}$ after 5 seconds?
Remember $r = 2$ from $2R \rightarrow P$

$$(1/[R_f]) = (1/[R_0]) + rkt$$

$$(1/[R_f]) = (1/0.1) + (2)(4)(5)$$

$$(1/[R_f]) = 50$$

$$[R_f] = 0.02$$

So after 5 seconds, 80% is gone