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Integrated Rate Laws

Finally a use for calculus!

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What is a rate?

It's a "delta/delta"!

Rate of reaction = $\frac{\Delta concentration}{\Delta time}$

In other words, it is a differential.

As you MAY recall from calculus, if you take a small enough delta (difference) you end up with a derivative!

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A rate as a derivative

Rate of reaction = $\frac{\Delta concentration}{\Delta time}$

If Δtime is small enough, we have:

$$Rate\ of\ reaction = \frac{-d[reactant]}{dt}$$

Why "-"? Because you are losing reactants and the rate should always be positive.

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Let's look at the rate law

Rate = k[A]

$$Rate\ of\ reaction = \frac{-d[A]}{dt} = k[A]$$

This is actually an integrable equation.

[Don't worry, this isn't a math class…it's just masquerading as one!]

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Solving the equation

I'll show you how to solve it, but it is only the solution that you need to know.

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

We collect the [A] on one side and get:

$$\frac{d[A]}{[A]} = -kdt$$

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Solving the equation

$$\frac{d[A]}{[A]} = -kdt$$

Now you can integrate both sides:

$$\int_{[A]_{initial}}^{[A]_{final}} \frac{d[A]}{[A]} = -\int_{time=0}^{final\ time} kdt$$

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Solving the equation

$$\int_{[A]_{initial}}^{[A]_{final}} \frac{d[A]}{[A]} = -\int_{time=0}^{final\ time} k dt$$

$$\ln[A]_{final} - \ln[A]_{initial} = -kt$$

This is the only equation we really need. This is called the “integrated rate law”…well, because we integrated the rate law. ☺

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What it means…

$$\ln[A]_{final} - \ln[A]_{initial} = -kt$$

What it means is that the concentration at any time decays logarithmically from the initial concentration. If I rearrange the equation a little:

$$\ln[A]_{final} = -kt + \ln[A]_{initial}$$

What does this look like to you?

Yes, it is the equation of a straight line (y=mx+b)!

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Using the integrated rate law

$$\ln[A]_{final} = -kt + \ln[A]_{initial}$$

If you know k and the initial concentration, you could calculate the concentration at any time.

For example, if I know k=0.015 s^{-1} and I start with 0.250 M A, how much A is left after 1 minute?

Beware the units. 1 minutes = 60 seconds. Since k is in s^{-1}, I need my time to be in seconds.

Plug and chug, baby!

$\ln[A]_{final} = -0.015 s^{-1} * 60\ s + \ln(0.250\ M)$

$\ln[A]_{final} = -2.286$

$[A]_{final} = e^{-2.286} = 0.102$ M

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Using the integrated rate law

$\ln[A]_{final} = -kt + \ln[A]_{initial}$

$\ln[A]_{final} = -0.015 s^{-1} * 60\ s + \ln(0.250\ M)$

$\ln[A]_{final} = -2.286$

$[A]_{final} = e^{-2.286} = 0.102\ M$

You can see the power of the integrated rate law. I can determine the remaining concentration of reactants at any second in time! (And, using stoichiometry, I could determine the concentration of products at any second in time!)

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Compare the integrated rate law to the rate law

$\ln[A]_{final} = -kt + \ln[A]_{initial}$

Rate = k[A]

For the same problem, the rate law only allows me to calculate the initial rate of the reaction:

Rate = $(0.015\ s^{-1})(0.250\ M) = 0.00375\ M/s$

I could also calculate the RATE for any specific concentration. But I can't know how long it takes me to get to that new concentration.

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Other uses of the integrated rate law

$\ln[A]_{final} = -kt + \ln[A]_{initial}$

It's a straight line. Scientists LOVE LOVE LOVE straight lines!

If you have a reaction that you KNOW is 1^{st} order, you could measure the [A] at a number of different times and plot the data and you'll get a straight line where the slope=-k. So you could use the equation to find the rate constant.

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For example, suppose I monitor [A]

Time (seconds)	[A] (M)
0	0.25
10	0.20
20	0.17
60	0.075

Since this is a first order reaction, the data should obey my integrated rate law.

So I plot the ln[A] vs time and I should get a straight line.

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For example, suppose I monitor [A]

Time (seconds)	[A] (M)
0	0.25
10	0.20
20	0.17
60	0.075

Since this is a first order reaction, the data should obey my integrated rate law.

So I plot the ln[A] vs time and I should get a straight line.

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For example, suppose I monitor [A]

Time (seconds)	[A] (M)	ln[A]
0	0.25	-1.386
10	0.20	-1.609
20	0.17	-1.772
60	0.075	-2.590

Now, I plot the last column against the first column and put the best fit straight line on it.

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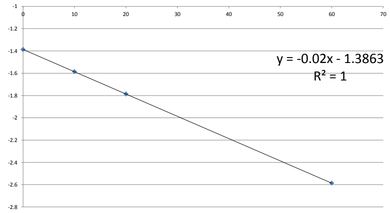
LOOK! IT'S A POINT! IT'S A PLANE! NO!!! IT'S A STRAIGHT LINE!



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So, what's the rate constant?

y = -0.02x - 1.3863

$\ln[A]_{final} = - kt + \ln[A]_{t=0}$

m= slope=-0.02
m=-k
k=-(-0.02)=0.02 s^{-1}

So, if I KNOW it's a 1st order reaction, I can make a graph to find the rate constant. I can also make a graph to find out IF it is 1st order.

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

Time (seconds)	$[H_2]$ (M)	$\ln[H_2]$
0	0.500	-0.69315
10	0.300	-1.20397
20	0.200	-1.60944
60	0.100	-2.30259

Now, I plot the last column against the first column and put the best fit straight line on it to see IF IF IF it is actually a straight line.

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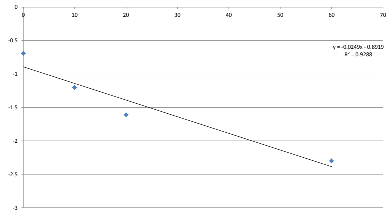
NOT a straight line – NOT a 1st order reaction!



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This works for other orders of reaction also.

For a second order reaction:

Rate = $k[A]^2$

You get an integrated rate law

$$\frac{1}{[A]_{final}} = kt + \frac{1}{[A]_{initial}}$$

Same idea, it's a straight line (y = mx+b) where:
Slope = k
Intercept = $\frac{1}{[A]_{initial}}$

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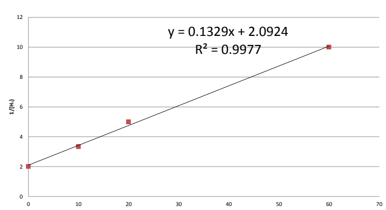
Hey! It's 2nd order!



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Also, there's the rare zeroth order

$$Rate = \frac{-d[A]}{d[t]} = k$$

If you integrate

$[A]_t$ = -kt + [A]

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Those are the easy ones

For more complicated mixed orders like:

Rate = k[A][B]

The math gets much more complicated, so we'll ignore them until you become a chemistry major. But you can do a similar thing.

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But a lot of reactions fall into those three categories.

0th order

$[A]_t$ = -kt + [A]

1st order

$\ln[A]_{final} = -kt + \ln[A]_{initial}$

2nd order

$\frac{1}{[A]_{final}} = kt + \frac{1}{[A]_{initial}}$

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How do we use this?

N_2 (g)+ 3 Cl_2(g)→ 3 NCl_3(g)

Given the following date, determine the rate law.

Time	$[N_2(g)]$ (M)
0 min	0.40
5 min	0.25
10 min	0.17
30 min	0.04
60 min	0.005

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GRAPH IT!

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Graph It!

N_2 (g)+ 3 Cl_2(g)→ 3 NCl_3(g)

Given the following date, determine the rate law.

Time	$[N_2(g)]$ (M)	$Ln([N_2])$	$1/[N_2]$
0 min	0.40	-0.916	2.5
5 min	0.25	-1.386	4.0
10 min	0.17	-1.772	5.88
30 min	0.04	-3.219	25
60 min	0.005	-5.298	200

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Try all 3 and see which one fits!

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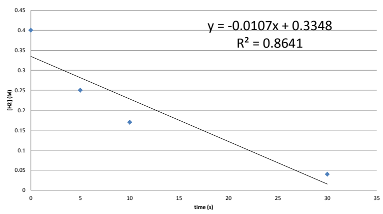
Not 1st order – unless it was a sloppy experiment



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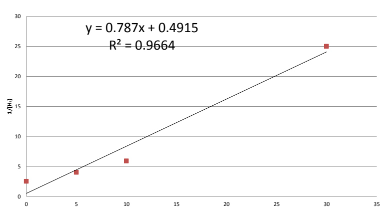
Maybe 2nd order – it's not a horrible fit.



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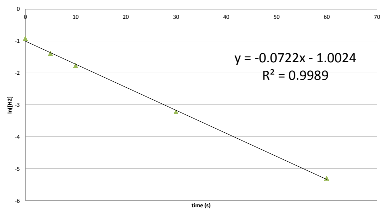
Hey, Goldilocks! It Fits 1[st] order!



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What if I don't have graph paper?

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What if I don't want to make a graph?

N_2 (g)+ 3 Cl_2(g)→ 3 NCl_3(g)

Given the following date, determine the rate law.

Time	$[N_2(g)]$ (M)
0 min	0.40
5 min	0.25
10 min	0.17
30 min	0.04
60 min	0.005

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3 possibilities

Rate = k

Rate = k$[N_2]$

Rate = k$[N_2]^2$

$$Rate = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\{[N_2]_{later\ time} - [N_2]_{earlier\ time}\}}{later\ time\ - earlier\ time}$$

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k is the rate CONSTANT and it's the slope of the line

0th order

$[A]_t = -kt + [A]$

1st order

$\ln[A]_{final} = -kt + \ln[A]_{initial}$

2nd order

$\frac{1}{[A]_{final}} = kt + \frac{1}{[A]_{initial}}$

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Slope is all over the place except 1st order

$N_2(g) + 3\,Cl_2(g) \rightarrow 3\,NCl_3(g)$

Given the following date, determine the rate law.

Time (min)	$[N_2(g)]$ (M)	slope– 0th order	slope - 1st order	K – 2nd order
0	0.40	$= \frac{-(0.25 - 0.40)}{5\ \text{min} - 0\ min} = 0.03\ M/min$	$\frac{-[\ln(0.25) - \ln(0.40)]}{5\ \text{min} - 0\ min} = 0.094$	$\frac{\frac{1}{0.25} - \frac{1}{0.40}}{5\ min} = 0.30$
5	0.25	0.016	0.077	0.376
10	0.17	0.0065	0.0723	0.96
30	0.04	0.00117	0.069	5.83
60	0.005			

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Problem recognition

What's the tell?

How do I know how to handle the problem?

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Method of initial rates – Rates measured for different initial mixes

The reaction:

$2\ I^-_{(aq)} + S_2O_8^{2-}{}_{(aq)} \rightarrow 6\ I_{2\ (aq)} + 2\ SO_4^{2-}(aq)$

was studied at 25° C. The following results were obtained for the rate of disappearance of $S_2O_8^{2-}$

$[I-]_0$ (M)	$[S_2O_8^{2-}]_0$ (M)	Initial rate (M/s)
0.080	0.040	12.5x10-6
0.040	0.040	6.25x10-6
0.080	0.020	6.25x10-6
0.032	0.040	5.00x10-6
0.060	0.030	7.00x10-6

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Integrated rate law – concentration at different times

$N_2\ (g) + 3\ Cl_2(g) \rightarrow 3\ NCl_3(g)$

Given the following date, determine the rate law.

Time	$[N_2(g)]$ (M)
0 min	0.40
5 min	0.25
10 min	0.17
30 min	0.04
60 min	0.005