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Sinde 1			
	Integrated Rate Laws		
	Finally a use for calculus!		
Slide 2		1	
	What is a rate?		
	It's a "delta/delta"! $ \text{Rate of reaction} = \frac{\Delta concentration}{\Delta time} $		
	Rate of reaction = ${\Delta time}$ 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!		
]	
		•	
Slide 3	A rate as a derivative] .	
	A rate as a derivative		
	Rate of reaction = $\frac{\Delta concentration}{\Delta time}$		
	If ∆time is small enough, we have: -d[reactant]		
	$Rate of reaction = \frac{-d[reactant]}{dt}$ Why ""? Recays you are being reactage, and the rate		
	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!]

Slide 5

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:

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

Slide 6

Solving the equation

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

Now you can integrate both sides:

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

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. ©

Slide 8

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)!

Slide 9

Using the integrated rate law

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

For example, if I know k=0.015 $s^{\cdot 1}$ 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 $s^{\text{-}1}$, I need my time to be in seconds.

Plug and chug, baby!
$$\begin{split} & \ln[A]_{final} = -0.015 s^{1.8} 60 \ s + \ln(0.250 \ M) \\ & \ln[A]_{final} = -2.286 \\ & [A]_{final} = e^{-2.286} = 0.102 \ M \end{split}$$

Using the integrated rate law

$$\begin{split} & \ln[A]_{final} = -kt + \ln[A]_{initial} \\ & \ln[A]_{final} = -0.015 s^{-1*} 60 \ s + \ln(0.250 \ M) \\ & \ln[A]_{final} = -2.286 \\ & [A]_{final} = e^{2.286} = 0.102 \ M \end{split}$$

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!)

Slide 11

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 = $(0.015~\mathrm{s}^{-1})[0.250~\mathrm{M})$ = $0.00375~\mathrm{M/s}$ 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.

Slide 12

Other uses of the integrated rate law

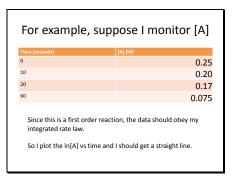
 $\ln[A]_{final} = -kt + \ln[A]_{initial}$

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

If you have a reaction that you KNOW is 1^{\pm} 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.

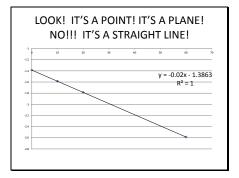
For example, suppose I monitor [A] Time (seconds) 0 0.25 10 0.20 20 0.17 60 0.075 Since this is a first order reaction, the data should obey my integrated rate law. So I plot the In[A] vs time and I should get a straight line.

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Time (seconds)	[A] (M)	In[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 the best fit straigh	column against the fin	st column and put

Slide 16



So, what's the rate constant?

y = -0.02x - 1.3863

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

m= slope=-0.02

m=-k

k=-(-0.02)=0.02 s⁻¹

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

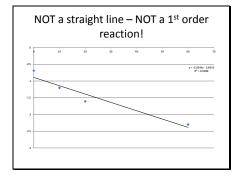
Slide 18

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

$2 H_2 + O_2 \rightarrow 2 H_2O$						
Time (seconds)	[H ₂] (M)	In[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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This works for other orders of reaction also.

For a second order reaction:

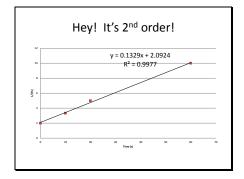
Rate = $k[A]^2$

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



Also, there's the rare zeroth order

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

If you integrate

$$\left[\mathsf{A}\right]_\mathsf{t} = -\mathsf{k}\mathsf{t} + \left[\mathsf{A}\right]$$

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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

 $\left[\mathsf{A}\right]_\mathsf{t} = -\mathsf{k}\mathsf{t} + \left[\mathsf{A}\right]$

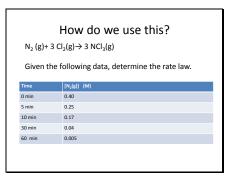
1st order

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

2nd order

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

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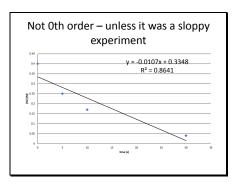
GRAPH IT!

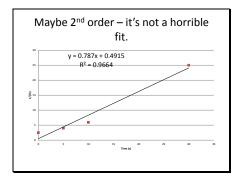
$\label{eq:Graph It!} Graph \ It!$ $N_2\left(g\right)+3\ Cl_2(g)\to 3\ NCl_3(g)$ Given the following data, determine the rate law.			
Time [I	N ₂ (g)] (M)	Ln((N ₂))	1/[N ₂]
0 min 0	0.40	-0.916	2.5
5 min 0	0.25	-1.386	4.0
10 min 0	0.17	-1.772	5.88
30 min 0	0.04	-3.219	25
60 min 0	0.005	-5.298	200

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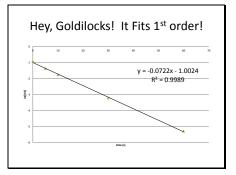
Try all 3 and see which one fits!

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Slide 31



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

- A. Find someone who can make a graph.
- B. Copy the answer from the person next to me.
- C. Calculate the rate of the reaction and see if the rate is constant or if the In(rate) is constant or 1/rate is constant.
- D. Calculate the slope between data points and see if they are constant.

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

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

Given the following data, determine the rate law.

Time	[N ₂ (g)] (W)
0 min	0.40
5 min	0.25
10 min	0.17
30 min	0.04
60 min	0.005

3 possibilities

 $\begin{aligned} & \text{Rate} = k \\ & \text{Rate} = k[N_2] \\ & \text{Rate} = k[N_2]^2 \\ & \\ & Rate = \frac{-\Delta[N_2]}{\Delta t} \\ & = \frac{-\{[N_2]_{later\ time} - [N_2]_{earlier\ time}\}}{2} \end{aligned}$

later time — earlier time

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

[A]_t = -kt + [A]

0th order

1st order

$$\begin{split} & \ln[A]_{final} \ \ _{=} \ _{-} kt + \ln[A] \ _{initial} \\ & \text{Or} \ ln \frac{[A]_{final}}{[A]_{initial}} = -kt \end{split}$$

nd order

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

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Slope is all over the place except $\mathbf{1}^{\text{st}}$

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– 0 th order	slope - 1 st order	K – 2 nd order
0	0.40	$= \frac{-(0.25 - 0.40)}{5 \min - 0 \min}$ $= 0.03 M/min$	$\frac{-[\ln(0.25) - \ln(0.40)]}{5 \min - 0 \min}$ = 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 ${\rm S_2O_8}^{2-}$

$[I-]_{\alpha}(M)$	$[S_2O_8^{2-}]_0(M)$	Initial rate (M/
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

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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Once I know the order, how's it work...?

Once I know the order of the reaction, I can use the integrated rate law to determine the concentration at any time.

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The following reaction is $\mathbf{1}^{\text{st}}$ order in Cl_2 and $\mathbf{1}^{\text{st}}$ order overall.

 $H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$

 $2~{\rm M~H_2}$ and $2~{\rm M~Cl_2}$ was placed in a $5~{\rm L~flask}$ at 298 K. The initial rate was $3.82{\rm x}10^{-3}~{\rm M/s}$. What was the rate after 10 minutes? How much HCl had been made after 10 minutes?

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As soon as I'm talking about TIME, it's an integrated rate law problem.

The order of the reaction was given. This actually tells me two things:

The Rate Law

The Integrated Rate Law

The following reaction is $\mathbf{1}^{\text{st}}$ order in Cl_2 and $\mathbf{1}^{\text{st}}$ order overall.

$$\mathsf{H_2}\left(\mathsf{g}\right) + \mathsf{Cl_2}\left(\mathsf{g}\right) \to 2\; \mathsf{HCl}(\mathsf{g})$$

 $Rate=k[Cl_2]$

Once I know that, the I.R.L. is automatic:
$$ln\frac{[Cl_2]_{time=t}}{[Cl_2]_{time=0}} = -kt$$

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 $Rate = k[Cl_2]$

$$ln\frac{[Cl_2]_{time=t}}{[Cl_2]_{time=0}} = -kt$$

Does this help me? What do I need to know?

Slide 45

The following reaction is $\mathbf{1}^{\text{st}}$ order in Cl_2 and $\mathbf{1}^{\text{st}}$ order overall.

$$\mathsf{H_2}\left(\mathsf{g}\right) + \mathsf{Cl_2}\left(\mathsf{g}\right) \to 2\; \mathsf{HCl}(\mathsf{g})$$

 $2~M~H_2~and~2~M~Cl_2~was~placed~in~a~5~L~flask~at~298~K.~ The initial rate was <math display="inline">3.82x10^{-3}~M/s.~What$ was the rate after 10 minutes? How much HCl had been made after 10 minutes?

lid		

 $Rate = k[Cl_2]$

$$ln\frac{[Cl_2]_{time=t}}{[Cl_2]_{time=0}} = -kt$$

Time=10 minutes $[H_2]_{initial} = 2M$ $[Cl_2]_{initial} = 2M$ $Rate_{initial} = 3.82x10^{-3} \text{ M/s}$

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3.82x10⁻³ M/s = k[2M] k=1.91x10⁻³ s⁻¹

This allows me to use the I.R.L.

$$ln\frac{[Cl_2]_{time=t}}{[Cl_2]_{time=0}} = -kt$$

$$\begin{split} \ln\frac{[Cl_2]_{time=t}}{[Cl_2]_{time=0}} &= -kt \\ \ln\frac{[Cl_2]_{time=t}}{2\,M} &= -(1.92\times 10^{-3}s^{-1})\;(600\,s) \\ \ln\frac{[Cl_2]_{10\,min}}{2M} &= -1.152 \\ \frac{[Cl_2]_{10\,min}}{2M} &= e^{-1.152} &= 0.316 \\ [Cl_2]_{10\,min} &= 0.632\,\mathrm{M} \end{split}$$

Slide 49		
	The following reaction is 1st order in Cl ₂ and 1st	
	order overall.	
	$H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$	
	2 M H ₂ and 2 M Cl ₂ was placed in a 5 L flask at	
	298 K. The initial rate was 3.82x10 ⁻³ M/s. What was the rate after 10 minutes? How much HCl	
	had been made after 10 minutes?	
		ı
		_
Slide 50		
	Rate = k[Cl ₂]	
	Rate = $1.92 \times 10^{-3} \text{ s}^{-1} (0.632 \text{ M}) = 1.2135 \times 10^{-3} \text{ M/s}$	
Slide 51]
Silue 31	How much HCI?	
	Just stoichiometry folks	
	I started with 10 moles Cl_2 : $\frac{2 mol}{L} \times 5 L = 10 moles initial$	
	I end up with:	
	$\frac{0.632 mol}{L} \times 5L = 3.16 mol left$	
	So 10 moles initial – 3.16 mol left = 6.84 mol reacted!	
	255C5 IIIIddi 5.10 IIIO ICIL - 0.04 IIIO ICatteu:	
		J

S	lide	52

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	$Cl_{2}(g) + H_{2}(g) = 2 HCl(g)$		
	$6.84\ mol\ {\it Cl}_2 reacted rac{2\ mol\ HCl}{1\ mol\ Cl_2}$		
	= 13.68 mol HCl		
ļ			