N9 - KINETICS

Rate Laws

Link to YouTube Presentation: https://youtu.be/0ghPS-QFc9c

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Rate Laws

Target: I can write differential rate laws and integrated rate laws, and I can use graphical methods to identify reaction orders.

Rate Laws

Differential rate laws

Express (reveal) the relationship between **concentration of reactants** and **rate of the reaction**.

- Usually just called **the rate law.**

Integrated rate laws

Express (reveal) the relationship between **concentration of reactants** and **time**

This section is review!

Only write stuff down if you need to! Or go back and add some notes to your notebook after class! We are going to zip through it since it is review!

Rate Laws

The rate law of a reaction is the mathematical relationship between the rate of the reaction and the concentrations of the reactants and homogeneous catalysts as well.

The rate law *must* be determined experimentally!

The rate of a reaction is directly proportional to the concentration of each reactant raised to a power.

Rate Laws

For the reaction **aA + bB → products** the rate law would have the form given below.

$$\boldsymbol{Rate = k[A]^n[B]^m}$$

Orders of the reactants - *n* and *m*
The rate constant - *k*

Rate Laws

The exponent on each reactant in the rate law is called the **order with respect to that reactant.**

Order of the reaction

The sum of the exponents on the reactants

Single Step Reactions

The orders do not match the coefficients in the balanced equation *UNLESS* the reaction happens in one single step.

Not as common as it taking multiple steps.

Single Step Reactions

The following reaction happens in one single step.

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

$$\text{Rate} = k[NO]^2[O_2].$$

The reaction is

- second order with respect to [NO],
- first order with respect to $[O_2]$,
- and third order overall.

Method of Initial Rates

Since we rarely know if a reaction happens in one or more steps, we have to use pattern recognition to figure out what the exponents must be.

- Systematically change the starting [ ]s of the various reactants while holding the [ ] of other reactants the same
- See how the rate changes as you change the [ ]s
  - What is the relationship between the rate and the [ ]s ?
  - That tells you the exponents!

Writing a (differential) Rate Law

Problem - Write the rate law, determine the value of the rate constant, k, and the overall order for the following reaction**:**

$$2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$$

Experiment	[NO] (mol/L)	[Cl_2] (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	11.4×10^{-6}

Use the Method of Initial Rates

Writing a (differential) Rate Law

Part 1 - Determine the values for the exponents in the rate law:

$2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$ Rate = $k[NO]^x[Cl_2]^y$

$4 = 2^x$

Experiment	[NO] (mol/L)	$[Cl_2]$ (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	11.4×10^{-6}

In experiment 1 and 2, $[Cl_2]$ is constant while [NO] doubles. Rate quadruples, so the rxn is 2nd order with respect to [NO]

$$\text{Rate} = k[NO]^2[Cl_2]^y$$

Writing a (differential) Rate Law

Part 1 - Determine the values for the exponents in the rate law:

$$2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$$

$$\text{Rate} = k[NO]^2[Cl_2]^y$$

$$2 = 2^y$$

Experiment	[NO] (mol/L)	$[Cl_2]$ (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	11.4×10^{-6}

Watch honors YouTube if you need a review on this!

In experiment 2 and 4, [NO] is constant while $[Cl_2]$ doubles. Rate doubles, so the reaction is first order with respect to $[Cl_2]$

$$\text{Rate} = k[NO]^2[Cl_2]^1$$

Writing a (differential) Rate Law

Part 2 - Determine the value of the rate constant, k, including units, by using any of the experimental trials – doesn't matter which one!

$2\ NO(g) + Cl_2(g) \rightarrow 2\ NOCl(g)$ **Rate = $k[NO]^2[Cl_2]^1$**

Experiment	[NO] (mol/L)	[Cl_2] (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}

$$1.43x10^{-6}\,\frac{mol}{L\cdot s} = k\left(0.250\,\frac{mol}{L}\right)^2\left(0.250\,\frac{mol}{L}\right)$$

$$k = \left(\frac{1.43x10^{-6}}{0.250^3}\right)\left(\frac{mol}{L\cdot s}\right)\left(\frac{L^3}{mol^3}\right) = \boxed{9.15x10^{-5}\,\frac{L^2}{mol^2\cdot s}}$$

How I like to find the units because I'm lazy ☺

We know the unit for rate is always M/sec, and we know the rate law, and that the units for [ ] is M

Rate = k[NO]^2[Cl$_2$]^1

$$\frac{M}{sec} = k\ x\ M^2 M^1$$

$$\cancel{\frac{M}{sec}}\ x\ \frac{1}{M^2}\ x\ \cancel{\frac{1}{M^1}} = k$$

$$\boxed{\frac{1}{M^2 sec} = k\ units}$$

$$\frac{L^2}{mol^2 sec} = k\ units$$

$$M^{-2} sec^{-1} = k\ units$$

$$L^2 mol^{-2} sec^{-1} = k\ units$$

Writing a (differential) Rate Law

Part 3 - Determine the overall order

The sum of the exponents, or orders, of the reactants.

$$R = k[NO]^2[Cl_2]$$

2 + 1 = 3

∴ The reaction is 3rd order

The Effect of Orders on Rate

$$\text{Rate} = k[A]^n$$

If you Double [A]	
Order	**Effect on Rate**
0	**No change**
1	**x 2**
2	**x 4**
3	**x 8**
1.5	*x ~2.83*
-1	*0.5*

Not common

This section is new!

For sure take notes on this part, and add more details at home like normal!

Integrated Rate Law

For the reaction A $\rightarrow$ products, the rate law depends on the concentration of A.

Applying calculus to integrate the rate law gives another equation showing the relationship between the **concentration of A** and the **time** of the reaction; this is called the **integrated rate law.**

Integrated Rate Law

Graphing Concentration Data vs Time			
Graph the following versus time. The one that is linear tells you the order! Why? Because of Math. Ha!			
Memory Device	**Y-axis**	**Order**	**y = mx + b format**
C *Concentration*	[A]	0^{th}	$[A]_t = -kt + [A]_0$
N *Natural Log*	Ln [A]	1^{st}	$Ln[A]_t = -kt + Ln[A]_0$
R *Reciprocal*	1/[A]	2^{nd}	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$

Half Life with Integrated Rate Laws

For 0th Order plug into: $[A]_t = -kt + [A]_0$

You get: $t_{1/2} = \dfrac{[A]_0}{2k}$

For 1st order plug into: $Ln[A]_t = -kt + Ln[A]_0$

You get: $t_{1/2} = \dfrac{0.693}{k}$

For 2nd order plug into: $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

You get: $t_{1/2} = \dfrac{1}{k[A]_0}$

Remember… half life is the time it takes for ½ the starting amount to decay.

So….if….

$$[A]t = \frac{[A]_0}{2}$$

Half Life with Integrated Rate Laws

Half-Life → $$[A]t = \frac{[A]_0}{2}$$

Order	Plug Into Integrated Law	You get….
0	$[A]_t = -kt + [A]_0$	$t_{1/2} = \frac{[A]_0}{2k}$
1	$Ln[A]_t = -kt + Ln[A]_0$	$t_{1/2} = \frac{0.693}{k}$
2	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$t_{1/2} = \frac{1}{k[A]_0}$

Relationship Between [ ] and ½ Life

- **0th Order –** Half-life is directly proportional to the [ ] of reactants
  Lower [ ] of reactants = shorter half-life (faster rate)

$$t_{1/2} = [A]_{init}/2k$$

- **1st Order -** Half-life is independent of the concentration.
  Always the same half-life no matter what [ ] of reactants – *Closest to true half-life*

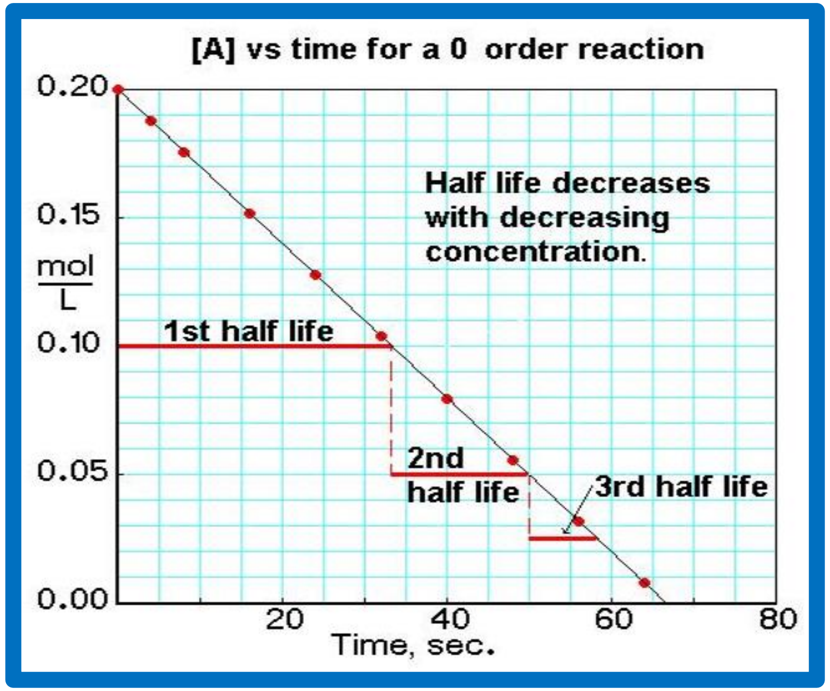
$$t_{1/2} = \ln(2)/k$$

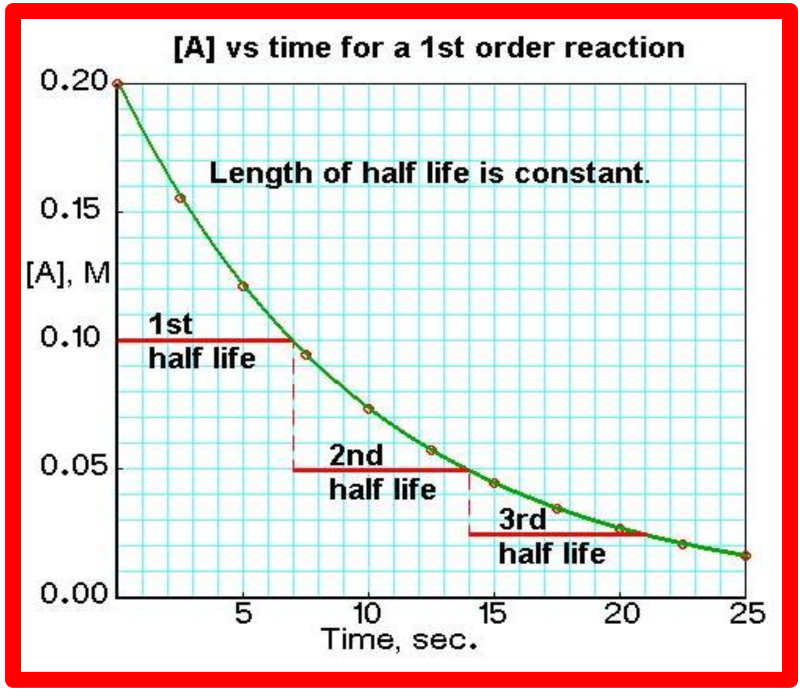
- **2nd Order -** Half-life is inversely proportional to the [ ] of reactants
  Lower [ ] of reactants = longer half-life (slower rate).

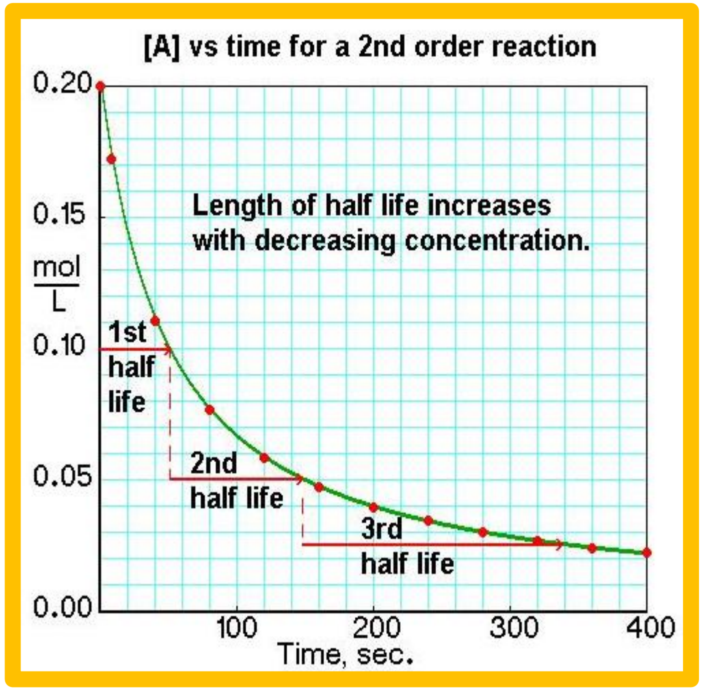
$$t_{1/2} = 1/(k[A]_{init})$$

How Does Half Life Change Over Time?

- **0th Order –** DECREASES as time goes on (faster rate)
- **1st Order –** CONSTANT as time goes on (radioactive decay!)
- **2nd Order –** INCREASES as time goes on (slower rate)





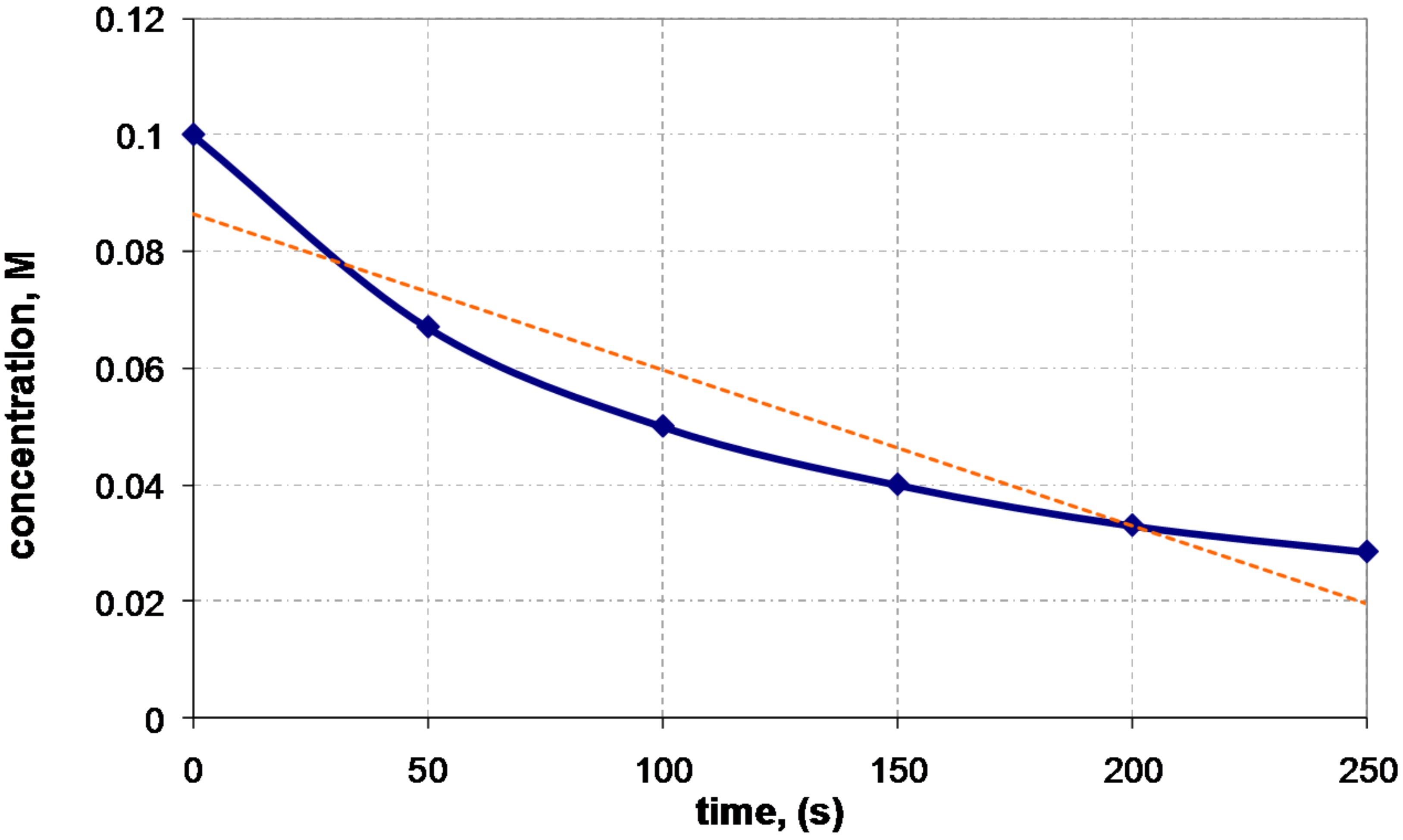


Graphical Determination of Rate Law

X-axis = Time			
Order	**Memory Device**		**Y-Axis**
0	**C**	**Concentration**	**[A]**
1	**N**	**Natural Logarithm**	**ln [A]**
2	**R**	**Reciprocal**	**1 / [A]**

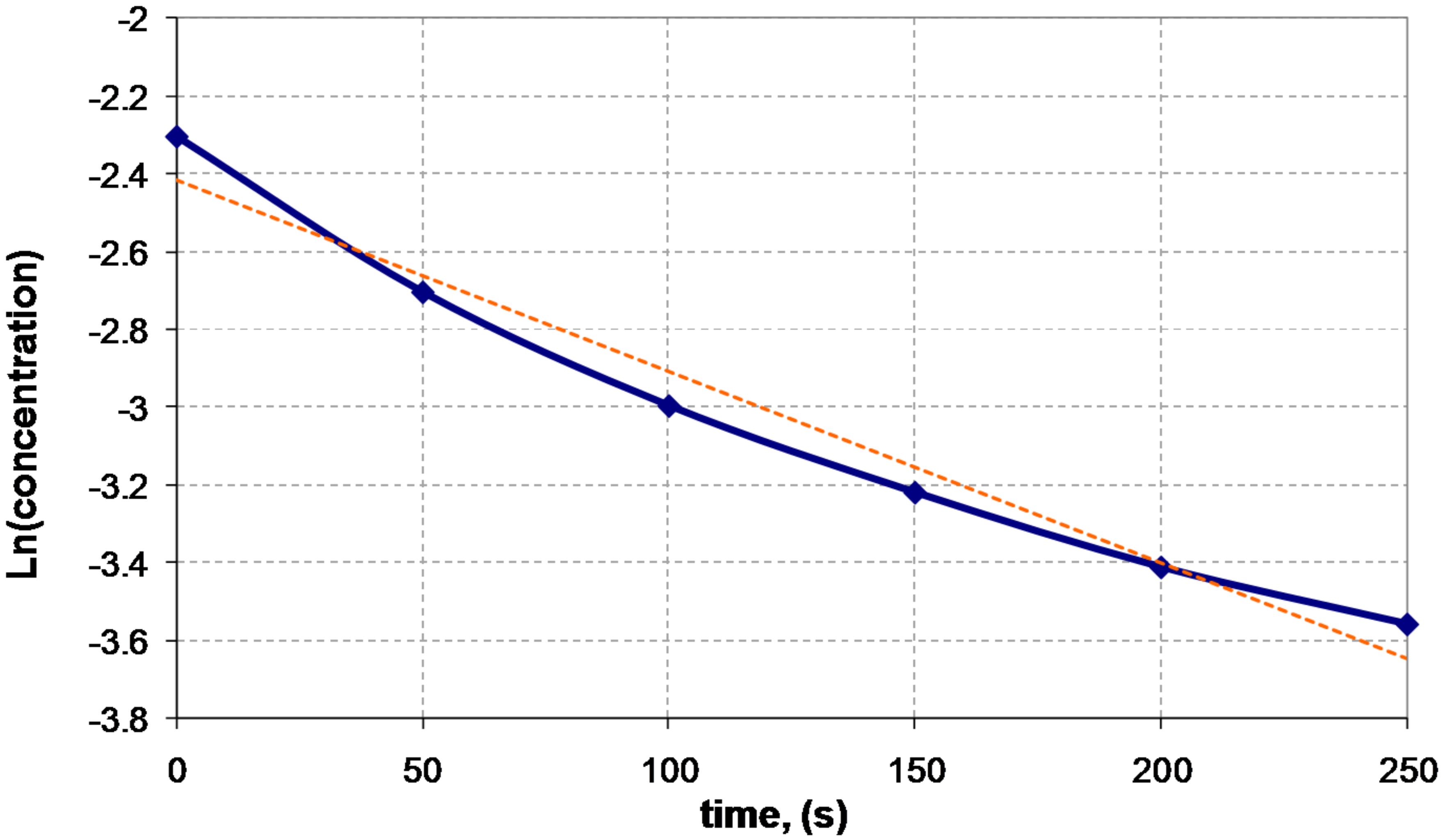
- Whichever plot gives a straight line determines the order with respect to [A].
  - If linear is [A] versus time, Rate = $k[A]^0$.
  - If linear is ln[A] versus time, Rate = $k[A]^1$.
  - If linear is 1/[A] versus time, Rate = $k[A]^2$.

[A] vs. Time



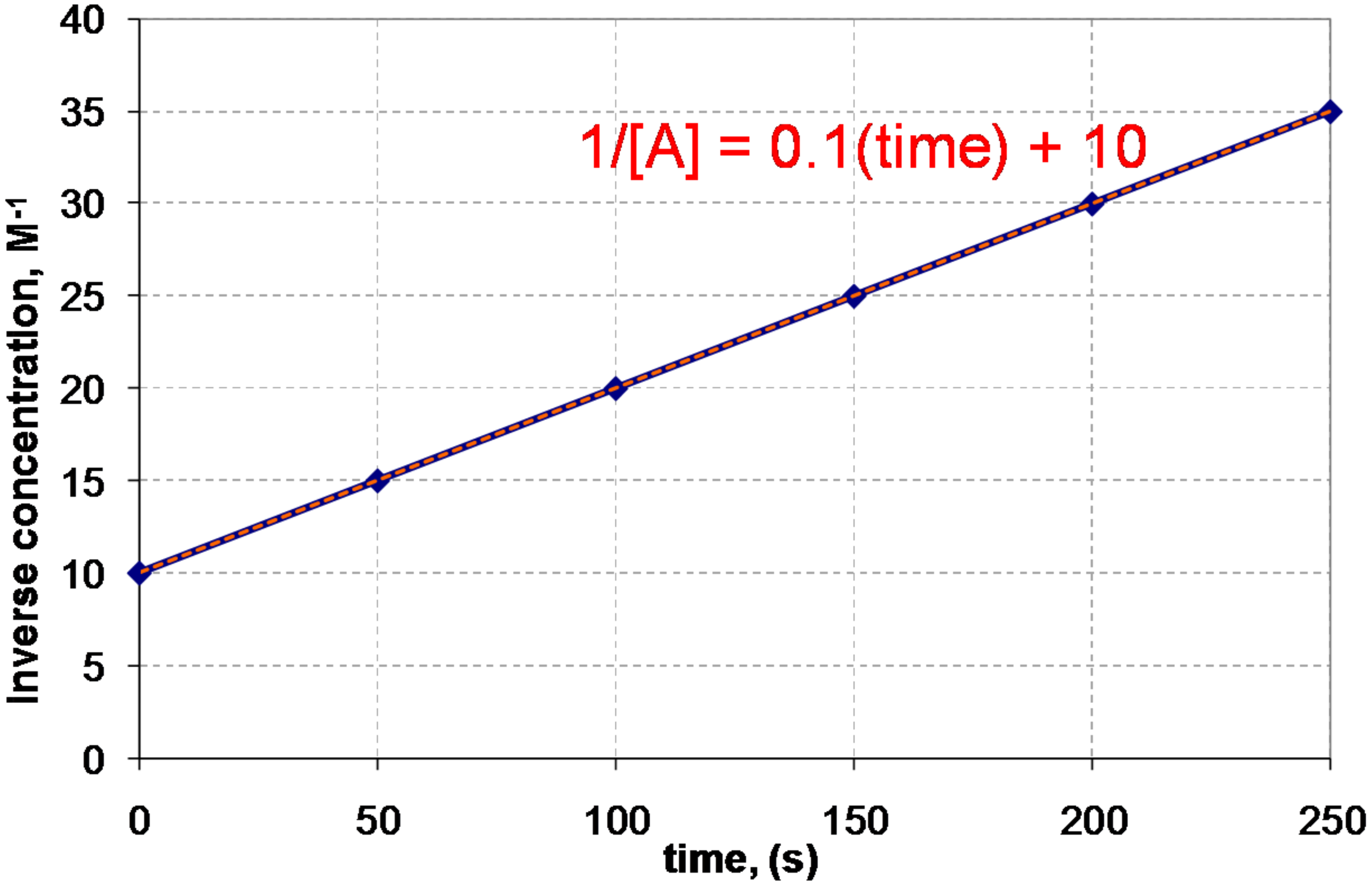
0.12
0.1
0.08
0.06
0.04
0.02
0
concentration, M
0
50
100
150
200
250
time, (s)

Ln [A] vs. Time



-2
-2.2
-2.4
-2.6
-2.8
-3
-3.2
-3.4
-3.6
-3.8
Ln(concentration)
0
50
100
150
200
250
time, (s)

1 / [A] vs. Time



R^2 = 0.999

R^2 tells you how good your of a fit your line is – perfect is R^2 = 1. The closer to 1 the better the fit!

How to Get an R^2 value?

Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.050

Excel or a graphing calculator!
Plug in the data!

Here is an Excel sheet I made to make the graphs. https://tinyurl.com/excel-kinetics

You can download Rate Law programs for the various brands/models of graphing calculators too.

Solving an Integrated Rate Law

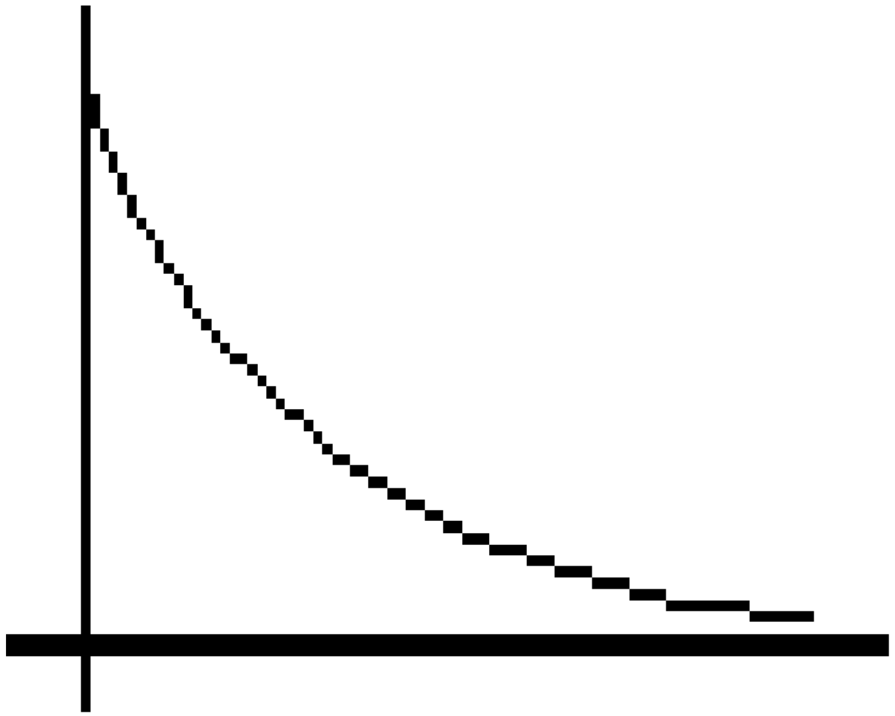
Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.050

Practice Problem:

Find the differential rate law, the integrated rate law and the value for the rate constant, k

Time vs. [H_2O_2]

Time (s)	[H_2O_2]
0	1.00
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.050



Regression results:

$y = ax + b$

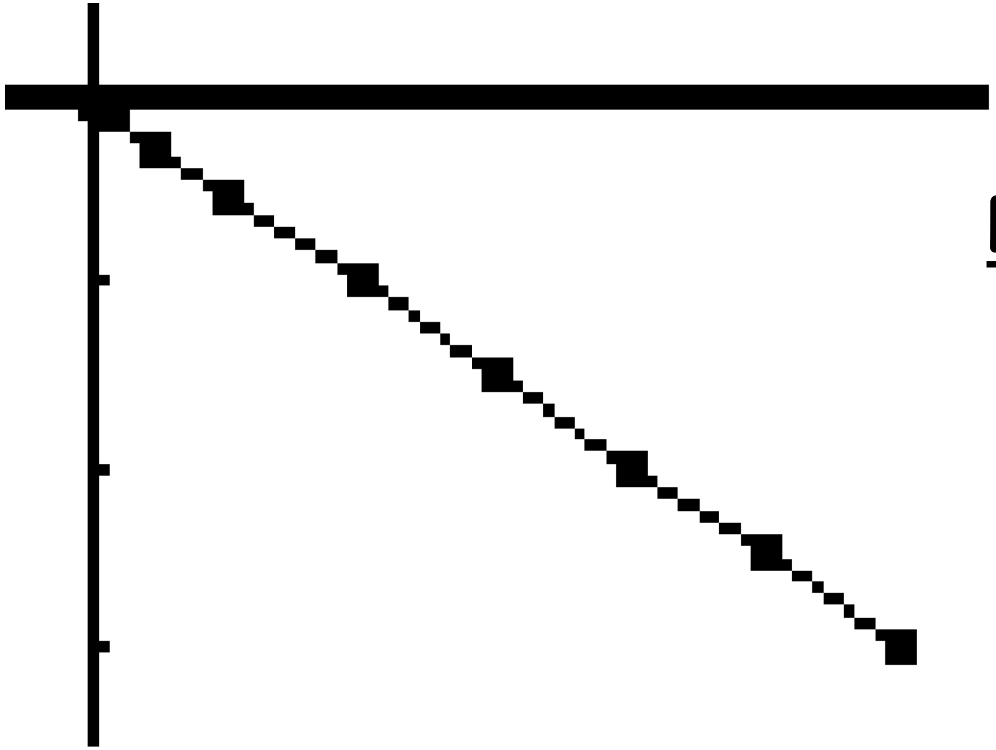
$a = -2.64 \times 10^{-4}$

$b = 0.841$

$r^2 = 0.8891$

Time vs. ln[H_2O_2]

Time (s)	ln[H_2O_2]
0	0
120	-0.0943
300	-0.2485
600	-0.5276
1200	-0.9943
1800	-1.514
2400	-2.04
3000	-2.501
3600	-2.996



Regression results:

$y = ax + b$

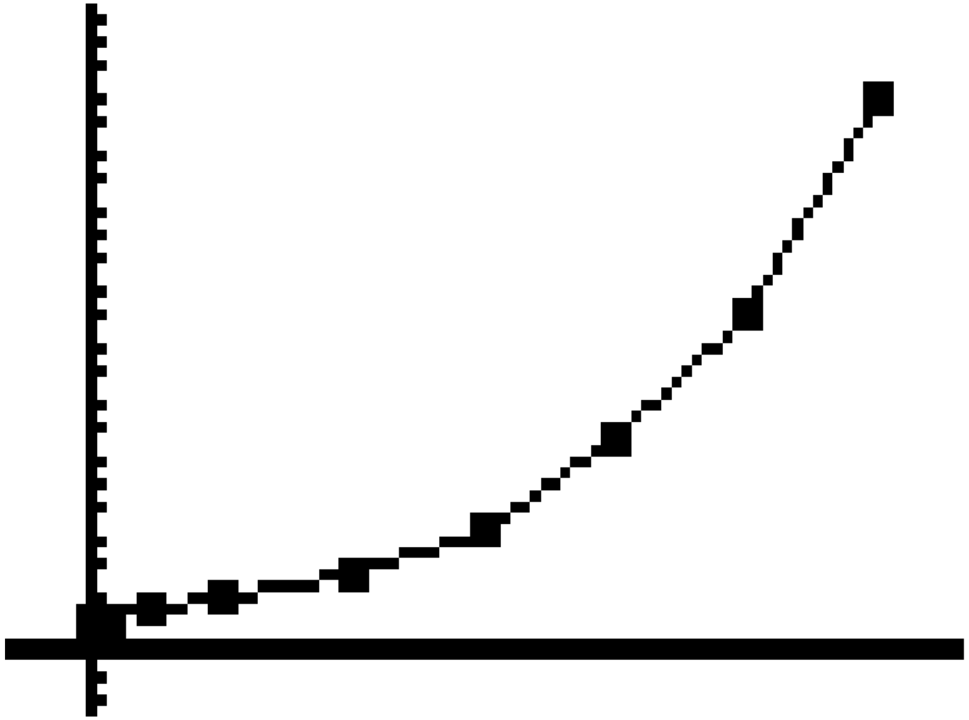
$a = -8.35 \times 10^{-4}$

$b = -.005$

$r^2 = 0.99978$

Time vs. 1/[H_2O_2]

Time (s)	1/[H_2O_2]
0	1.00
120	1.0989
300	1.2821
600	1.6949
1200	2.7027
1800	4.5455
2400	7.6923
3000	12.195
3600	20.000



Regression results:

$y = ax + b$

$a = 0.00460$

$b = -0.847$

$r^2 = 0.8723$

<u>And the winner is…</u> Time vs. $\ln[H_2O_2]$

1. **As a result, the most linear line (best R^2 value) for the reaction is Ln[A] therefore...** **1st order!**

2. **The (differential) rate law is:**

$$R = k[H_2O_2]$$

3. **The integrated rate law is:**

$$\ln[H_2O_2] = -kt + \ln[H_2O_2]_0$$

4. **But…what is the rate constant, *k* ?**

Finding the Rate Constant, k

Method #1: Calculate the slope from the Time vs. ln[H_2O_2] table.

$$slope = \frac{\Delta \ln[H_2O_2]}{\Delta t} = \frac{-2.996}{3600\,s}$$

$$slope = -8.32\,x10^{-4}\,s^{-1}$$

Time (s)	ln[H_2O_2]
0	0
120	-0.0943
300	-0.2485
600	-0.5276
1200	-0.9943
1800	-1.514
2400	-2.04
3000	-2.501
3600	-2.996

Now remember:

$$\ln[H_2O_2] = -kt + \ln[H_2O_2]_0$$

∴ k = -slope

$$\boxed{k = 8.32 \times 10^{-4}\ s^{-1}}$$

Finding the Rate Constant, k

Method #2: Obtain k from the linear regression analysis.

$$slope = a = -8.35\,x10^{-4}\,s^{-1}$$

Now remember:

$$\ln[H_2O_2] = -kt + \ln[H_2O_2]_0$$

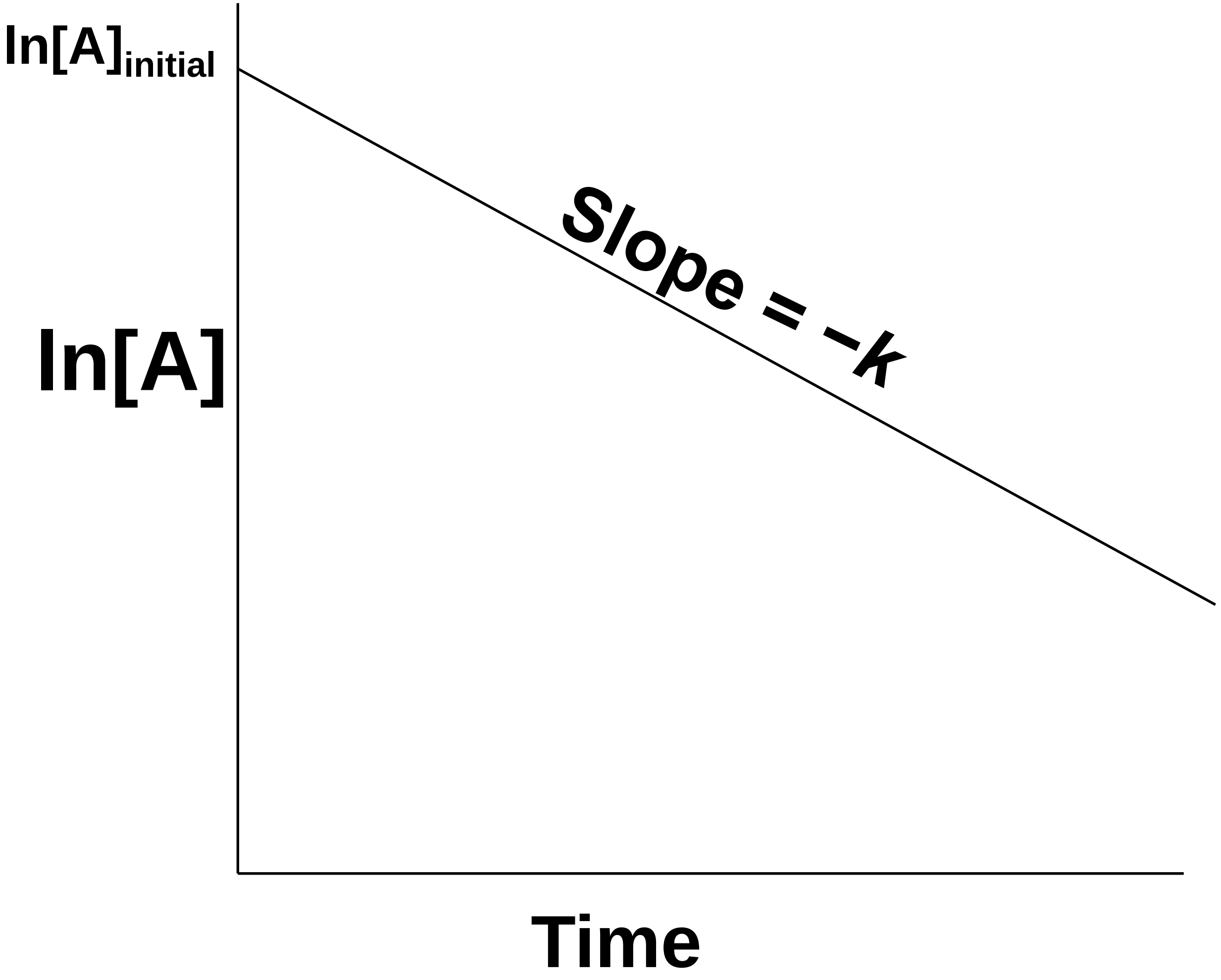
$\therefore$ k = -slope

$$\boxed{k = 8.35 \times 10^{-4} s^{-1}}$$

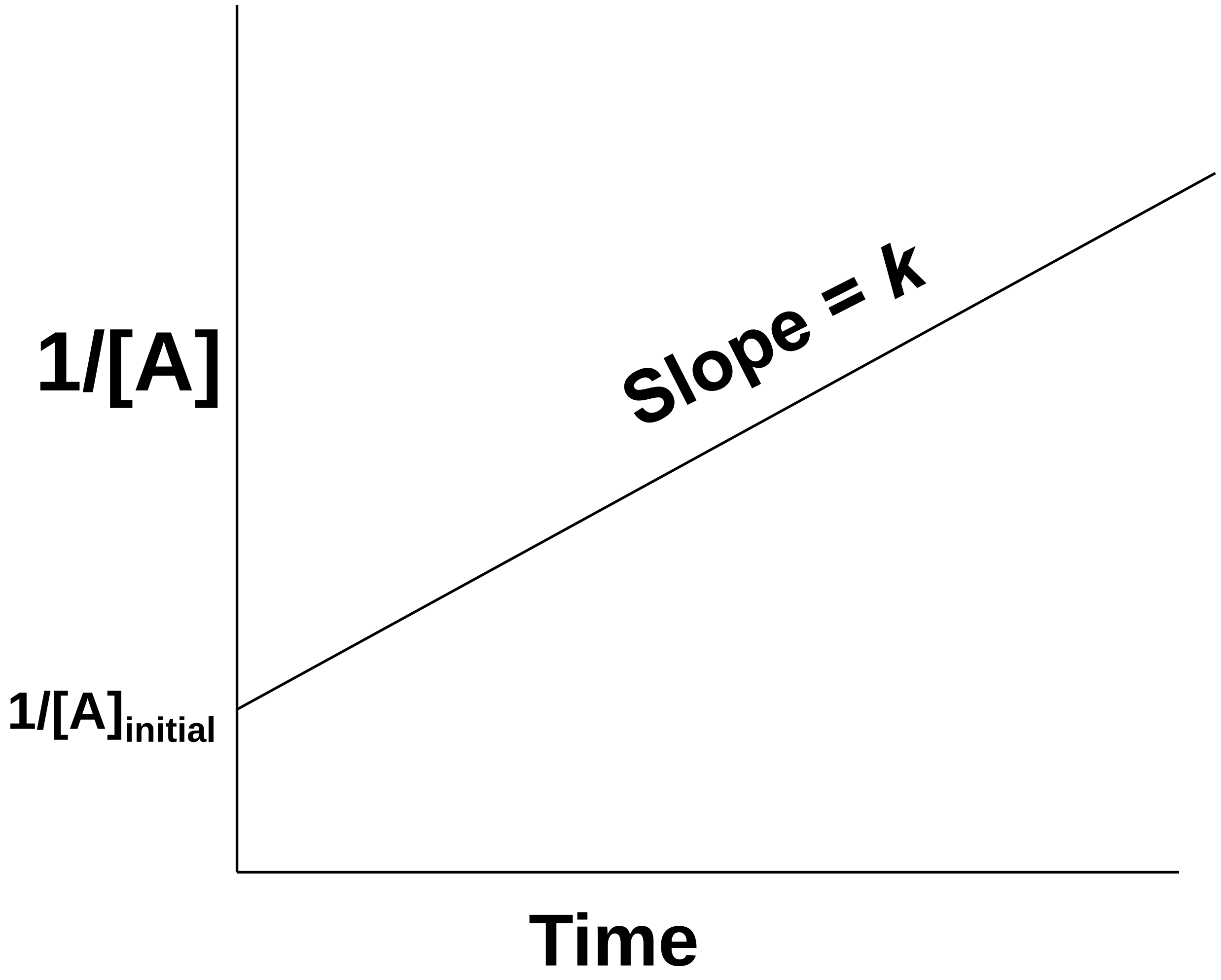
Regression results:

y = ax + b
a = -8.35 x 10^{-4}
b = -.005
r^2 = 0.99978

1st Order – Integrated Rate Law



2^{nd} Order – Integrated Rate Law



Integrated Rate Laws w/ more than 1 reactant

Too hard! We need a way to simplify it!

Examine rate w/ one reactant very low [ ] and the others **much** higher

- Rate = $k[A]^n[B]^m[C]^p$

  – [A] **much** lower than [B] and [C] ([B]> >[A] and [C] > >[A])

  – Then [B] and [C] do not change as much relative to [A] so… they don’t really matter!

$$\text{Rate} = k'[A]^n$$

(**analogy** – Billionaire giving away $500, won’t feel it much.
Mrs. Farmer giving away $500 will feel it a lot more

Integrated Rate Laws w/ more than 1 reactant

Simplifies the Rate Law into something we can more easily measure and figure out

$$\text{Rate} = k[A]^n[B]^m[C]^p \quad \rightarrow \quad \text{Rate} = k'[A]^n$$

We call this process

Pseudo-(1st/2nd/3rd etc..) order rate law

- Simplification yields a rate law of a particular order
- The Prime means pseudo

YouTube Link to Presentation

https://youtu.be/0ghPS-QFc9c