KINETICS

Rate Laws

Rate Laws

Differential rate laws - express (reveal) the relationship between concentration of reactants and rate of the reaction.

- The differential rate law is usually just called **the rate law.**

Integrated rate laws express (reveal) the relationship between concentration of reactants and time

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 $\rightarrow$ products** the rate law would have the form given below.

$$Rate = k[A]^n[B]^m$$

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.

<u>Single Step Reactions</u>

The following reaction happens in one single step.

2 NO(g) + O$_2$(g) → 2 NO$_2$(g)

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) → 2 NOCl(g)

Experiment	[NO] (mol/L)	[Cl$_2$] (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43 x 10^{-6}
2	0.500	0.250	5.72 x 10^{-6}
3	0.250	0.500	2.86 x 10^{-6}
4	0.500	0.500	11.4 x 10^{-6}

Method of Initial Rates

Writing a (differential) Rate Law

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

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

$$Rate = k[NO]^x[Cl_2]^y$$

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]

$$Rate = k[NO]^2[Cl_2]^y$$

Writing a (differential) Rate Law

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

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

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}

In experiment 2 and 4, [NO] is constant while [Cl$_2$] doubles. Rate doubles, so the reaction is first order with respect to [Cl$_2$]

$$Rate = k[NO]^2[Cl_2]^1$$

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) → 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 x 10^{-6}

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

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

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

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

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

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

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

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

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

Writing a (differential) Rate Law

Part 3 - Determine the overall order

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

$$R = k[NO]^2[Cl_2]$$
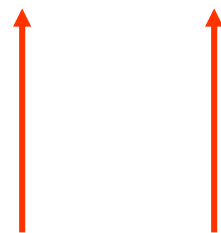
2 + 1 = 3

∴ The reaction is 3rd order

The Effect of Orders

$$Rate = k[A]^n$$

If you Double [A]	
Order	**Effect on Rate**
0	**No change**
1	**x 2**
2	**x 4**
3	**x 9**
1.5	*x ~2.83*
-1	*0.5*

Not common

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]	0th	$[A]_t = -kt + [A]_0$
N *Natural Log*	Ln [A]	1st	$Ln[A]_t = -kt + Ln[A]_0$
R *Reciprocal*	1/[A]	2nd	$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

Half Life with Integrated Rate Laws

If $[A]t = \dfrac{[A]_0}{2}$,   then plug into $[A]_t = -kt + [A]_0$

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

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

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

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

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

Half Life with Integrated Rate Laws

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

Relationship Between [ ] and ½ Life

- **0th Order -**Lower the initial [   ] of reactants, the shorter the half-life.

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

- **1st Order -** Half-life is independent of the concentration.
  - *Closest to true half-life*

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

- **2nd Order -** Half-life is inversely proportional to the initial [   ] increasing the initial concentration shortens the half-life.
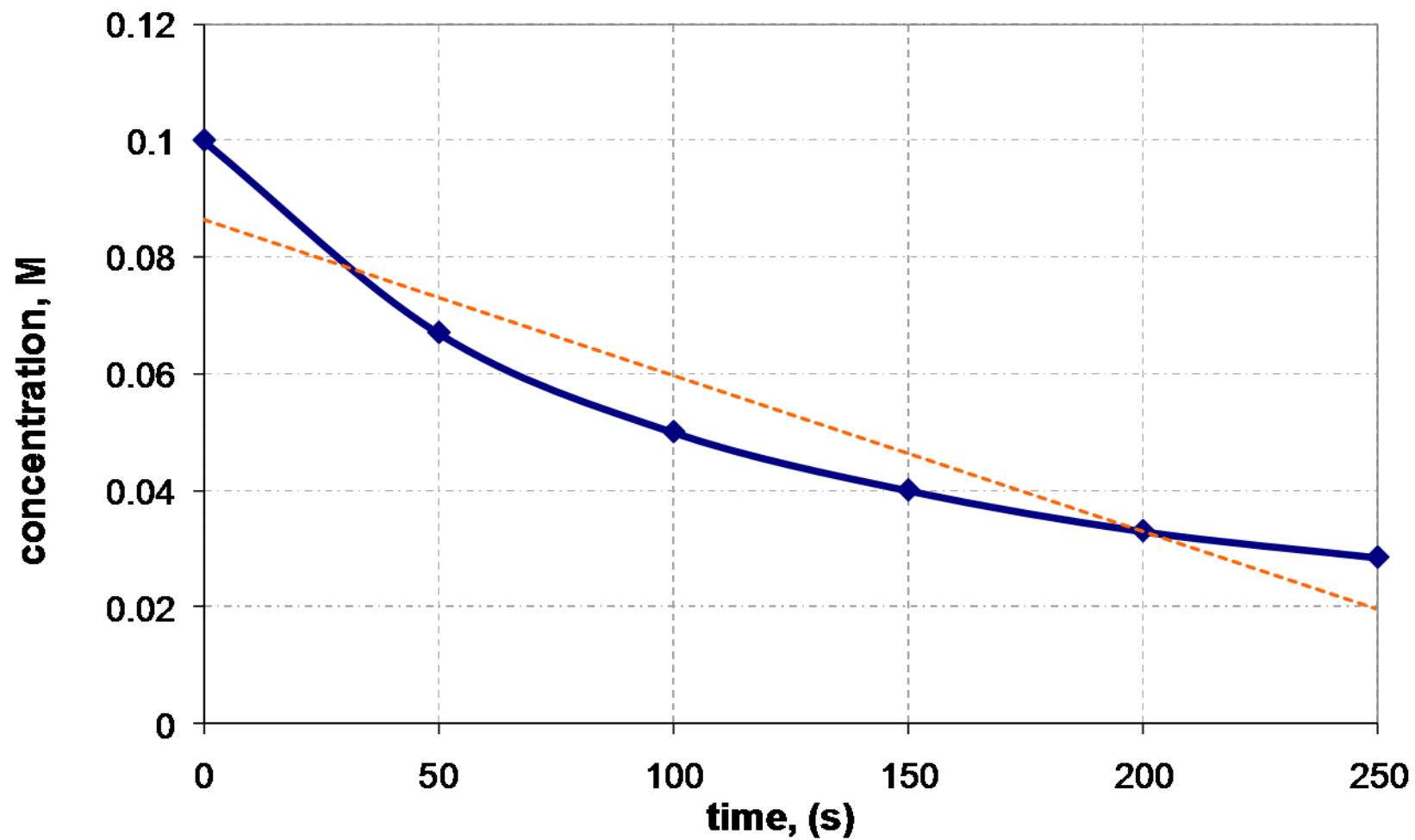
$$t_{1/2} = 1/(k[A]_{init})$$

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.
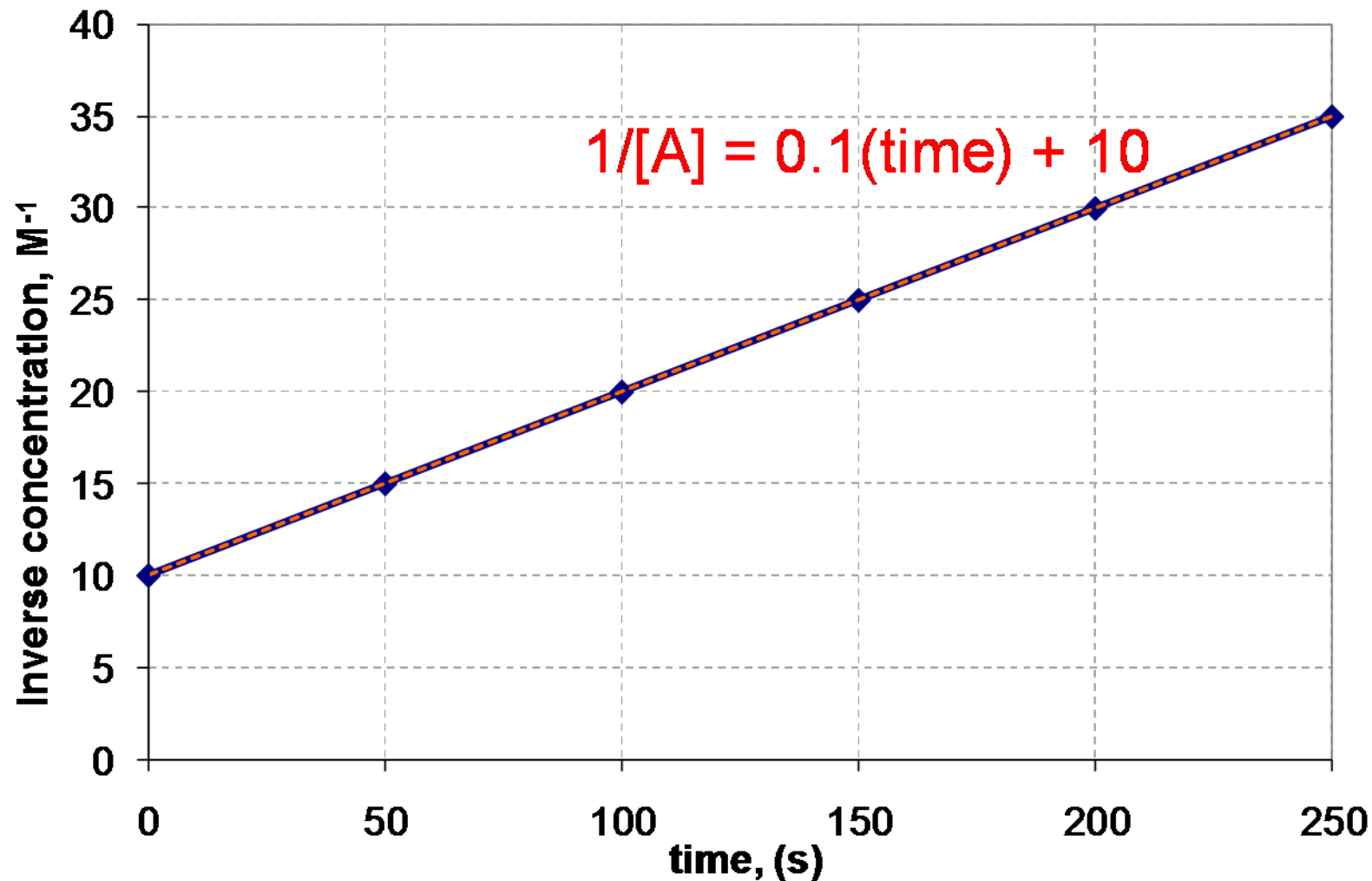 - If linear is 1/[A] versus time, Rate = k[A]^2.

[A] vs. Time

Ln [A] vs. Time

1 / [A] vs. Time

$1/[A] = 0.1(time) + 10$
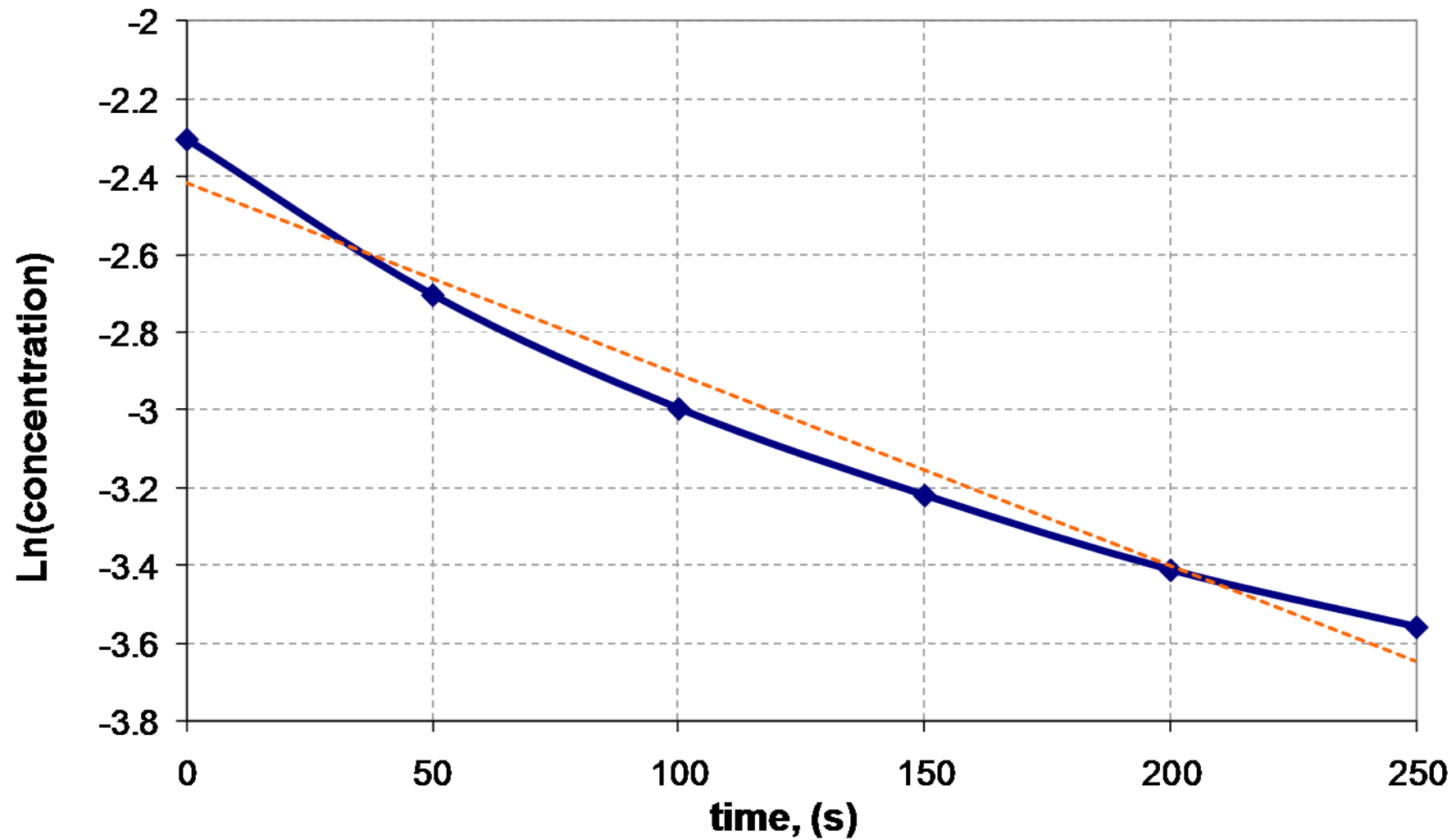
$R^2 = 0.999$

R^2 tells you how good your of a fit your line is – perfect is R2 = 1. The closer to 1 the better the fit!

Solving an Integrated Rate Law

Time (s)	[H$_2$O$_2$] (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

Problem: Find the integrated rate law and the value for the rate constant, k

Excel or a graphing calculator really help! 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.

Time vs. [H$_2$O$_2$]

Time (s)	[H$_2$O$_2$]
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
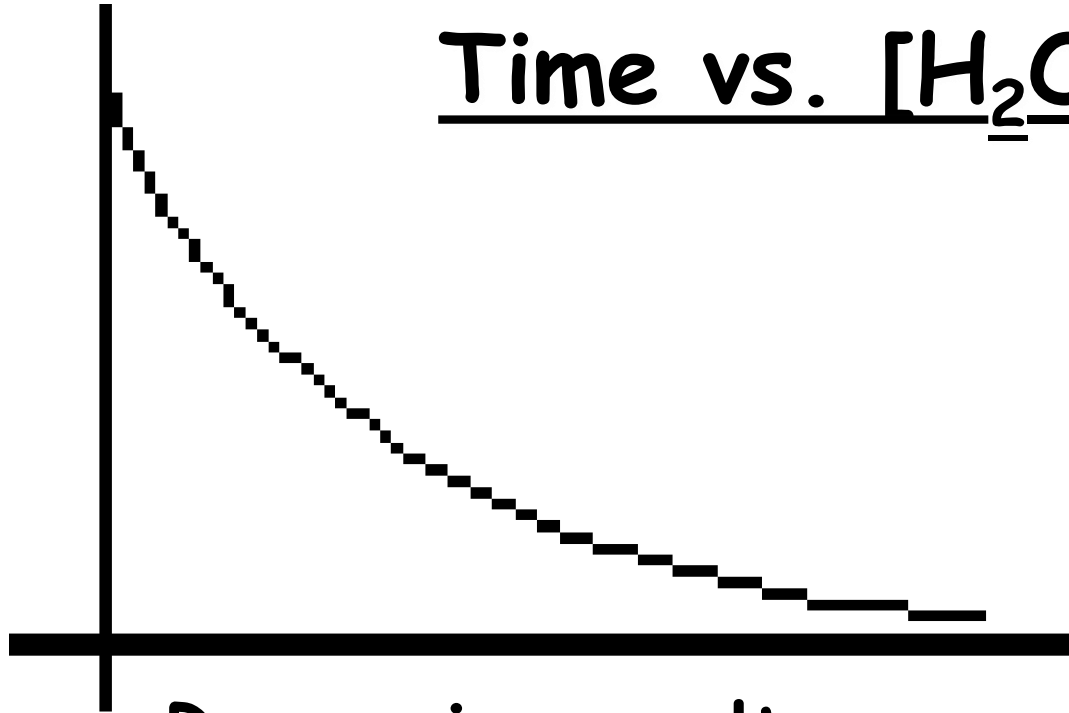
Regression results:

y = ax + b
a = -2.64 x 10^{-4}
b = 0.841
r^2 = 0.8891

Time vs. ln[H₂O₂]
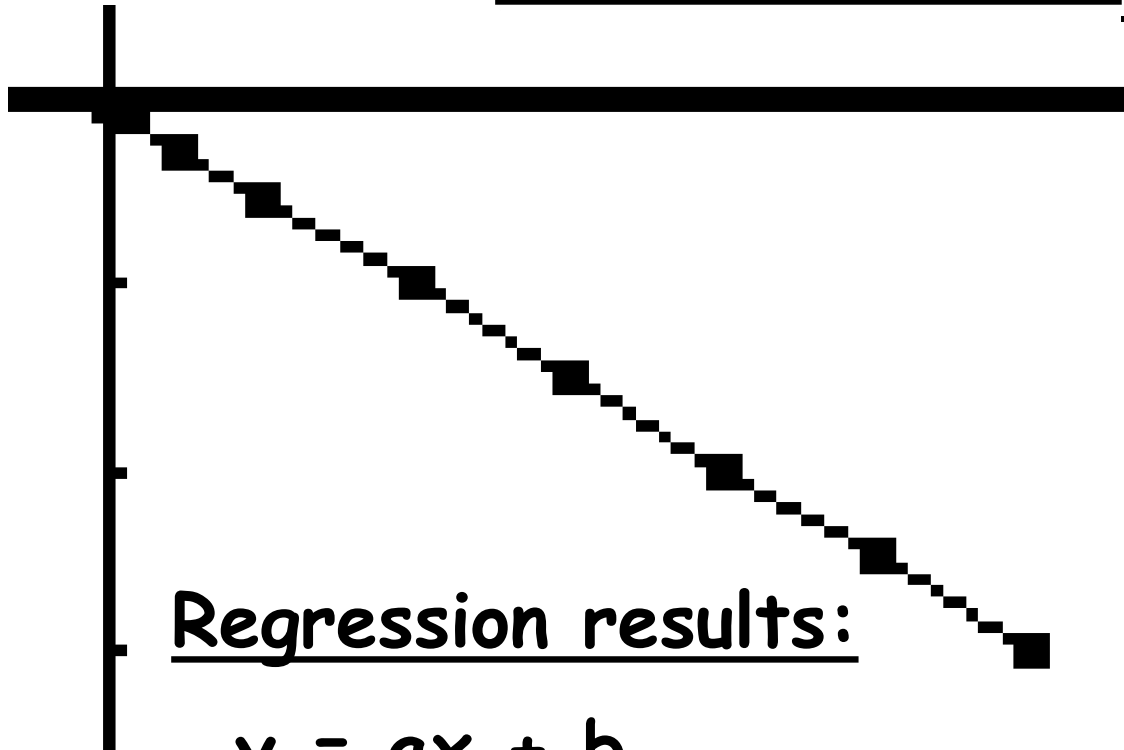
Regression results:

$y = ax + b$

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

$b = -.005$

$r^2 = 0.99978$

Time (s)	ln[H₂O₂]
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

Time vs. 1/[H₂O₂]
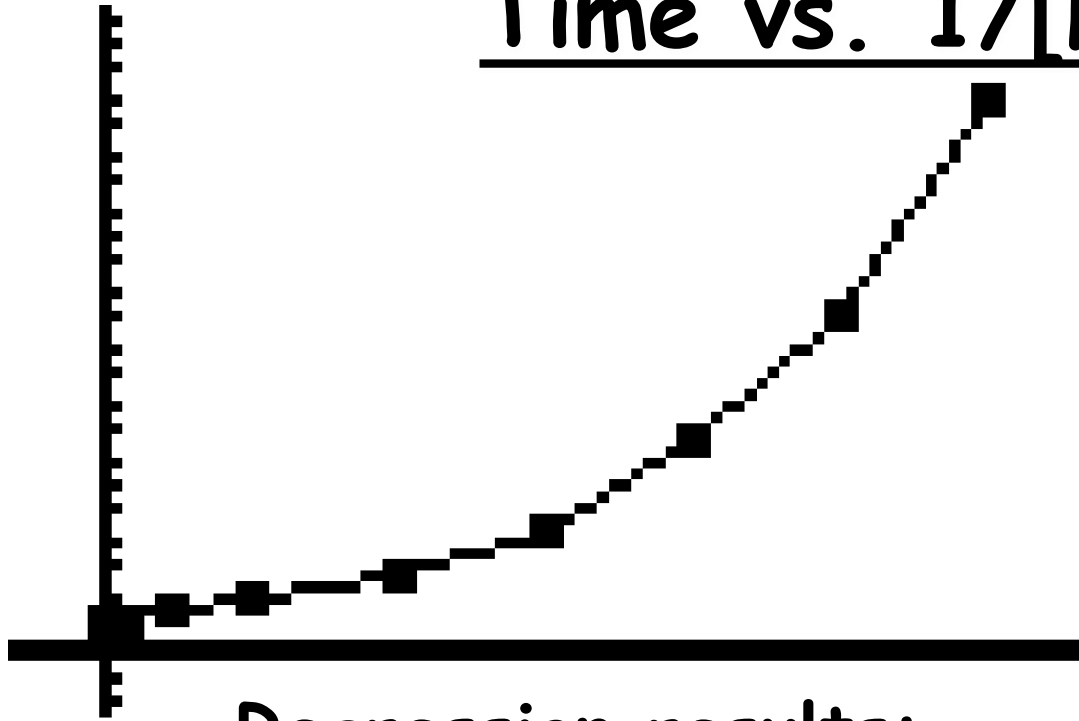
Regression results:

$y = ax + b$

$a = 0.00460$

$b = -0.847$

$r^2 = 0.8723$

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

And the winner is… Time vs. ln[H₂O₂]

1. As a result, the reaction is **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.

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

$$slope = -8.32\,x\,10^{-4}\,s^{-1}$$

Now remember:

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

$\therefore$ **k = -slope**

k = 8.32 x 10^{-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

Finding the Rate Constant, k

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

$$slope = a = -8.35\,x\,10^{-4}\,s^{-1}$$

Now remember:

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

$\therefore$ **k = -slope**

k = 8.35 x 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

$\ln[A]_{initial}$

$\ln[A]$

Slope = –k

Time
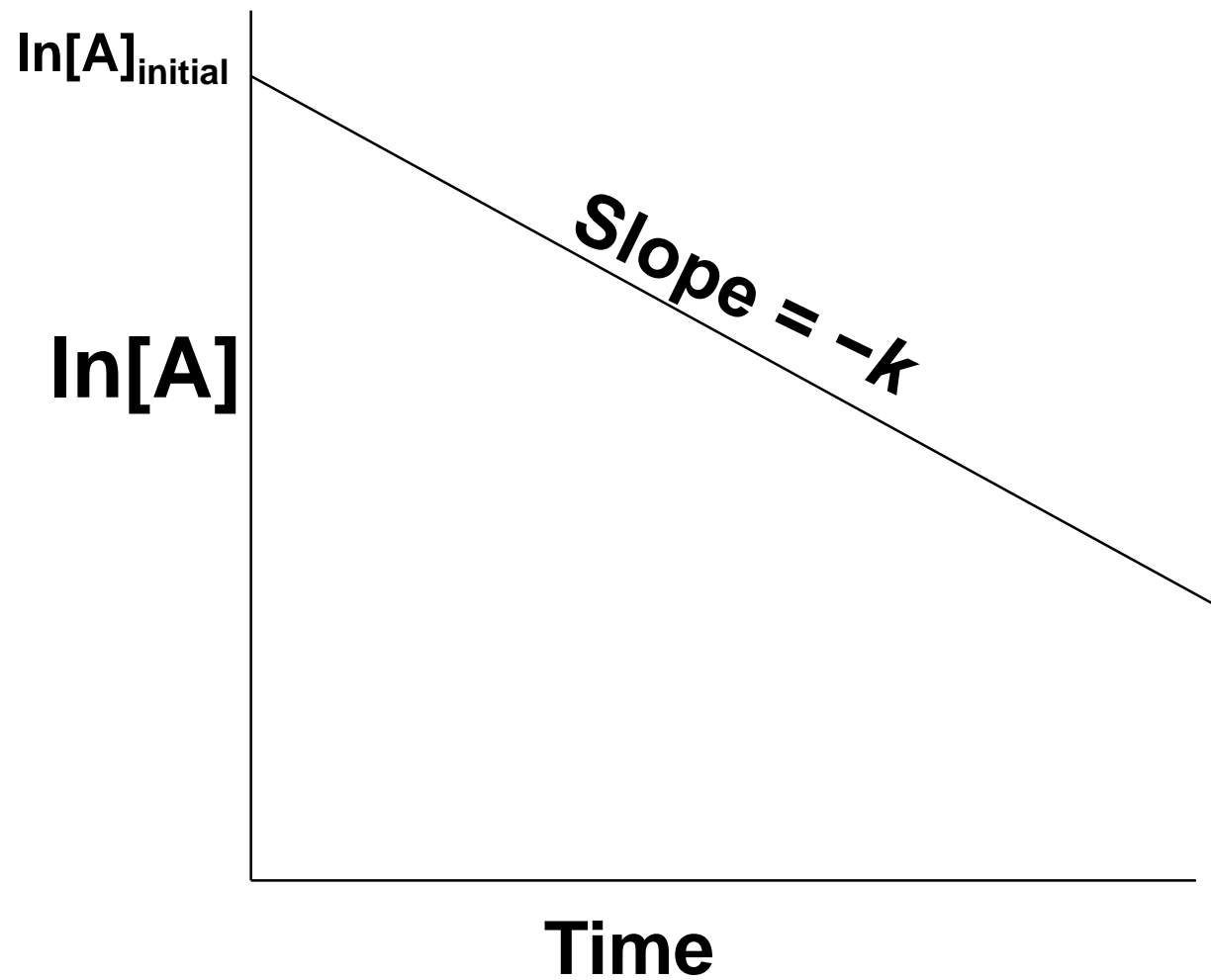
2nd Order – Integrated Rate Law
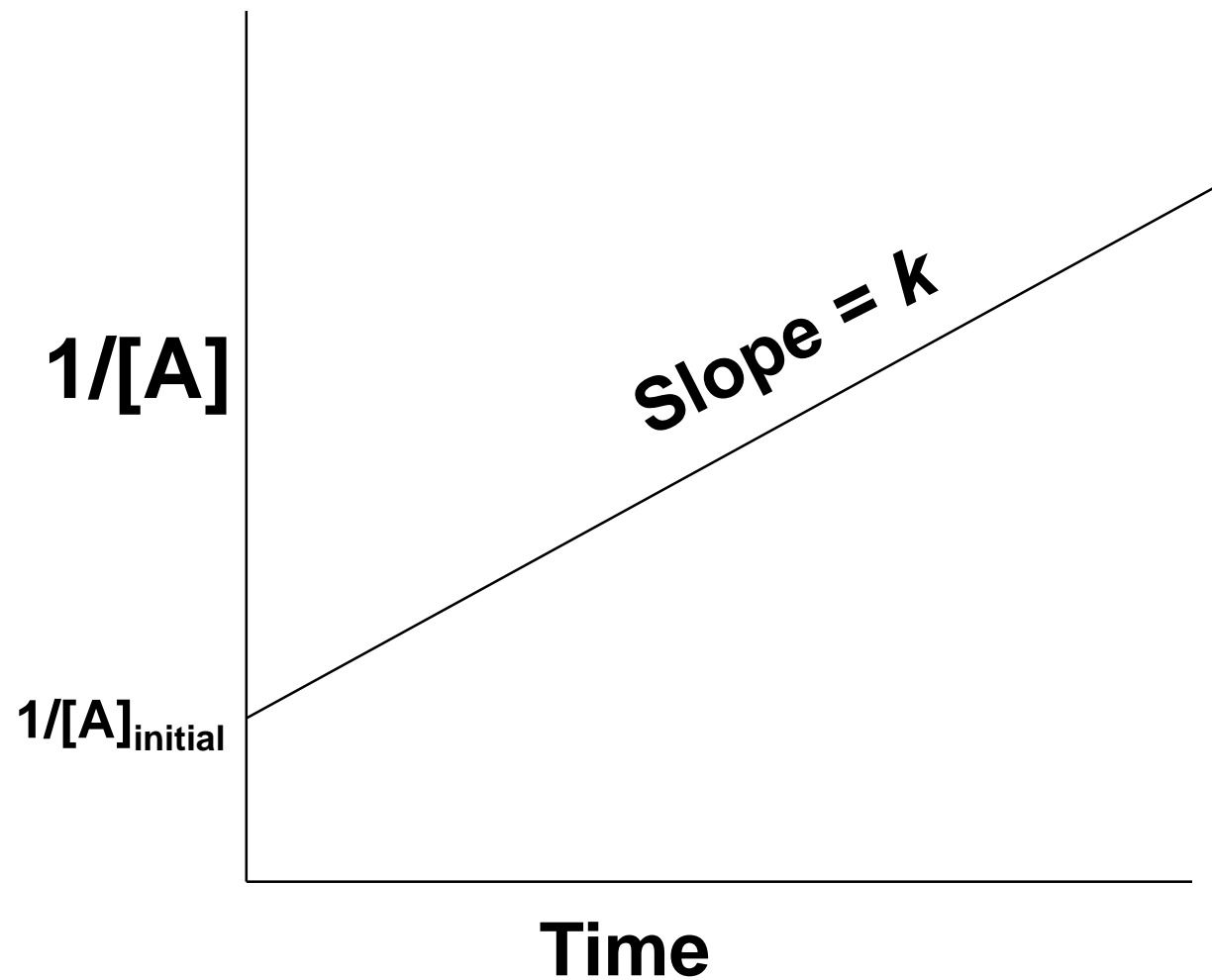
Integrated Rate Laws w/ more than 1 reactant

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

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

  – If $[B] >> [A]$ and $[C] >> [A]$ then $[B]$ and $[C]$ do not change as much relative to $[A]$ so…they don't really matter!

    – Rate = $k'[A]^n$

- **Pseudo-first-order rate law** (or zero-order , or second-order)
  - Simplification yields a rate law of a particular order
  - The Prime means pseudo