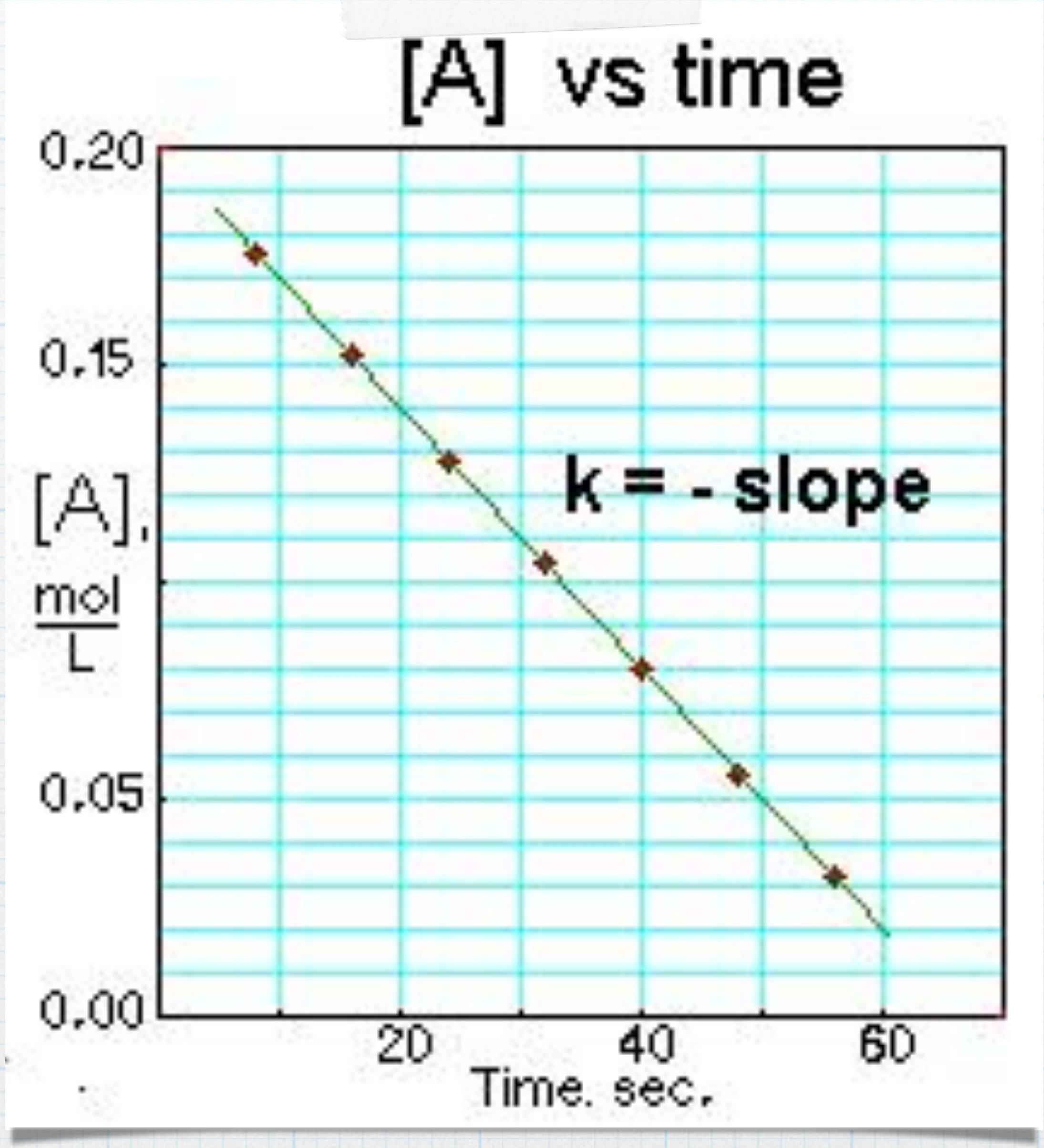
Rate Law and Order Reactions

First Order Reactions

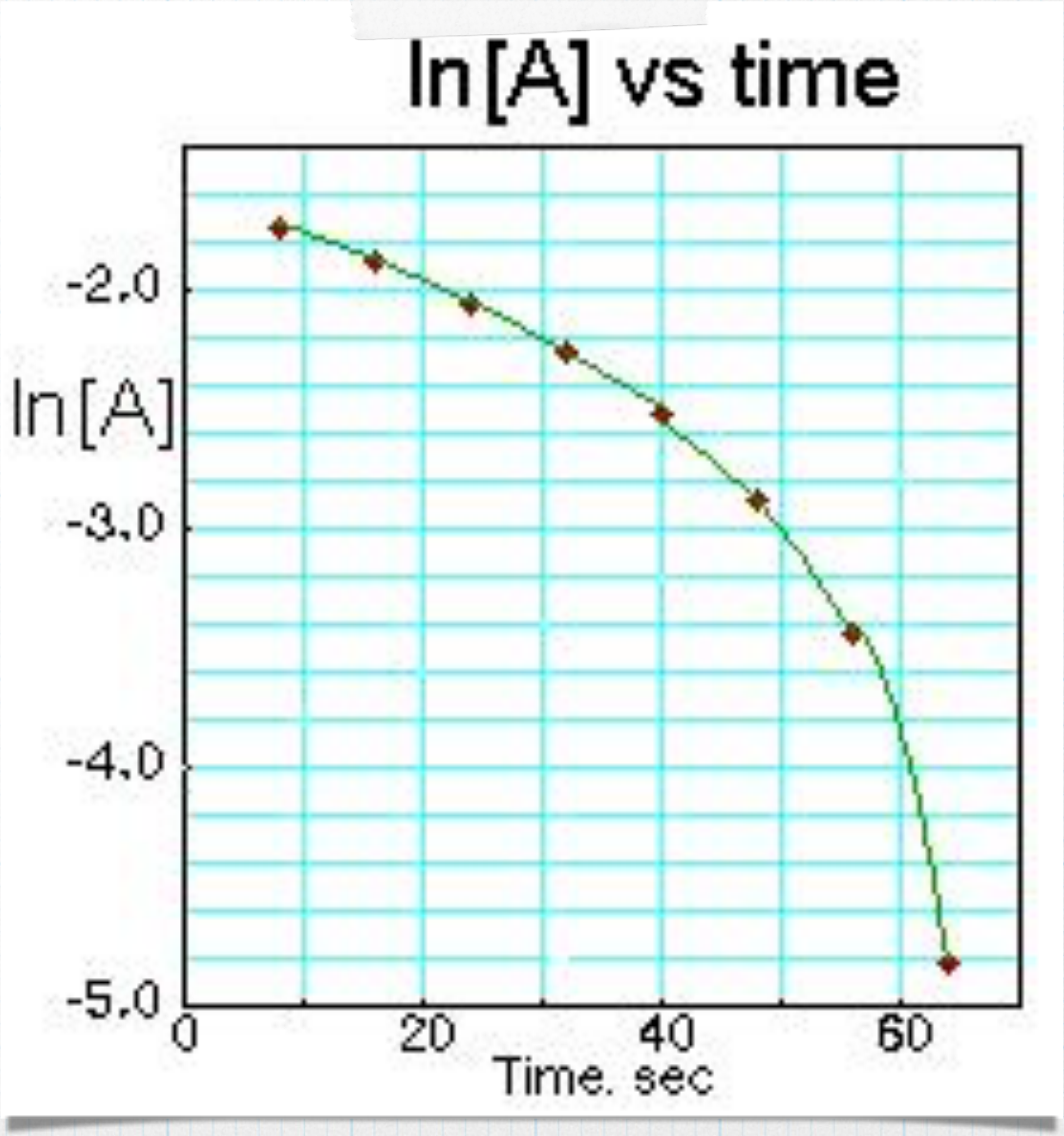
* A reaction in which rate is linear
    * k is used to represent the rate constant
    * rate = k[A]



Second Order Reaction

* Rate of reaction better fits a parabolic curve

  * rate = k $[A]^2$



Quantitative Effects of Factors

* The mathematical relationship between the reaction rate and the factors that affect it is called the RATE LAW.
* The rate law may not be predicted theoretically. It must be determined experimentally.

Quantitative Effects of Factors

* To determine experimentally, the concentration of on reactant is changed while the other remains the same.
* The rate of chemical reaction is then measured and recorded.

Rate Laws

* The rate law is proportional to the product of the initial concentrations of the reactants to some exponential values

$$rate = k\,[A]^m\,[B]^n$$

A and B are reactants

m = order of the reaction with respect to A

n = order of the reaction with respect to B

k = rate constant

m+n is the overall order of the reaction

How to Determine Order

First Order	Second Order
If m = 1, the rxn is 1st order wrt reactant A	If m = 2, the rxn is 2nd order wrt reactant A
When [A] is doubled, rate doubles	When [A] is doubled, rate quadruples
When [A] is tripled, the rate triples	When [A] is tripled, the rate is nine times faster

How to Determine Rate Constant

The rate constant can be determined from any experimental data using the following equation:

$$k = \frac{rate}{[A]^m[B]^n}$$

Example

* You are told that experimental evidence gives you the following rate law equation:
    * Rate = k $[A]^1[B]^2[C]^0$

Example

* Rate = k $[A]^1[B]^2[C]^0$
* What happens if the concentration of A is doubled?
* What happens if the concentration of B is tripled?
* What happens if the concentration of C is multiplied by four?

Example

* Rate = k $[A]^1[B]^2[C]^0$
* What happens if the concentration of A is doubled? **Rate doubles**
* What happens if the concentration of B is tripled? **Rate multiplied by nine**
* What happens if the concentration of C is multiplied by four? **Rate stays the same**

Example

- The following reaction is studied experimentally
  - $2NO_{(g)} + 2H_{2(g)} \rightarrow Ns(g) + 2H_2O_{(g)}$
- Data reveals that doubling nitrogen monoxide results in a fourfold increase, where doubling hydrogen only doubles reaction rates.
- The data from a concentration time graph shows the slow of the tangent is 0.25 M/s, [NO]=0.1M and $[H_2]$= 0.04 M.

Solution

* First we can determine order:
  * rate= k $[NO]^2[H_2]$

Solution

* Now substitute in graph data
    * rate= k $[NO]^2[H_2]$ where

Rate = 0.25
$[NO]$ = 0.1 M
$[H_2]$ = 0.04 M

Solution

* Now substitute in graph data
  * rate= k $[NO]^2[H_2]$ where

Rate = 0.25
[NO] = 0.1 M
$[H_2]$ = 0.04 M

$0.25 = k\,[0.1]^2[0.04]$
$k = (0.25)/[(0.1)^2(0.04)]$
$k = 625\ M^{-2}/sec$

Solution

* Now substitute in graph data
    * rate= k $[NO]^2[H_2]$ where

Rate = 0.25
[NO] = 0.1 M
$[H_2]$ = 0.04 M

$0.25 = k\,[0.1]^2[0.04]$
$k = (0.25)/[(0.1)^2(0.04)]$
$k = 625\ M^{-2}/sec$

So our full rate equation would be rate=625$[NO]^2$[H2]

Challenge Yourself!

* Chlorine dioxide reacts with hydroxide ions to produce a mixture of chlorate and chlorite ions.

$$2ClO_{2(aq)} + 2OH^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + ClO_2^-{}_{(aq)} + H_2O_{(l)}$$

Experiment	[ClO2]	[OH]	Rate
1	0.015	0.025	1.30×10^{-3}
2	0.015	0.05	2.60×10^{-3}
3	0.045	0.025	1.16×10^{-2}

Use this information to find k

$$rate = k [ClO_3]^m [OH]^n$$

$$rate = k[ClO_3]^m[OH]^n$$

Determine m

$$\frac{r_3 = k[ClO_3]^m[OH]^n}{r_1 = k[ClO_3]^m[OH]^n}$$

$$\frac{1.6 \times 10^{-2} = k(0.0450)^m(0.0250)^n}{1.3 \times 10^{-3} = k(0.0150)^m(0.0250)^n}$$

$$rate = k [ClO_3]^m [OH]^n$$

Determine m

$$\frac{r_3 = k [ClO_3]^m [OH]^n}{r_1 = k [ClO_3]^m [OH]^n}$$

$$\frac{1.6 \times 10^{-2} = \cancel{k}(0.0450)^m \cancel{(0.0250)^n}}{1.3 \times 10^{-3} = \cancel{k}(0.0150)^m \cancel{(0.0250)^n}}$$

$$9 = (3)^m$$

$$m = 2$$

$$rate = k[ClO_3]^m[OH]^n$$

Determine m

$$\frac{r_3 = k[ClO_3]^m[OH]^n}{r_1 = k[ClO_3]^m[OH]^n}$$

$$\frac{1.6 \times 10^{-2} = k(0.0450)^m (0.0250)^n}{1.3 \times 10^{-3} = k(0.0150)^m (0.0250)^n}$$

$$9 = (3)^m$$

$$m = 2$$

Determine n

$$\frac{r_2 = k[ClO_3]^m[OH]^n}{r_2 = k[ClO_3]^m[OH]^n}$$

$$\frac{2.6 \times 10^{-3} = k(0.0150)^m (0.0500)^n}{1.3 \times 10^{-3} = k(0.0150)^m (0.0250)^n}$$

$$rate = k[ClO_3]^m[OH]^n$$

Determine m

$$\frac{r_3 = k[ClO_3]^m[OH]^n}{r_1 = k[ClO_3]^m[OH]^n}$$

$$\frac{1.6 \times 10^{-2} = k(0.0450)^m (0.0250)^n}{1.3 \times 10^{-3} = k(0.0150)^m (0.0250)^n}$$

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$$\frac{r_2 = k[ClO_3]^m[OH]^n}{r_2 = k[ClO_3]^m[OH]^n}$$

$$\frac{2.6 \times 10^{-3} = k(0.0150)^m (0.0500)^n}{1.3 \times 10^{-3} = k(0.0150)^m (0.0250)^n}$$

$$2 = (2)^n$$

$$n = 1$$

$$rate = k\,[ClO_3]^{2}\,[OH]^{1}$$

$$k = \frac{rate}{[A]^{m}[B]^{n}}$$

$$rate = k[ClO_3]^2[OH]^1$$

$$k = \frac{rate}{[A]^m[B]^n}$$

Determine k

$$k = \frac{rate}{[ClO_3]^2[OH]^1}$$

$$k = \frac{1.30 \times 10^{-3} \text{ mol/Ls}}{[0.0150 \text{ mol/L}]^2[0.0250 \text{ mol/L}]^1}$$

$$k = 231 \text{ L}^2/\text{mol}^2\text{s}$$