

April 22, 2002

➤ Exam #3

- ✓ Solution Key is now online
- ✓ Graded exams will be returned later this week

➤ Kinetics

- ✓ Assigned problems now online

✓ Labs

ALL LABS DUE NO LATER THAN:

MIDNIGHT, MAY 1st

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The Method of Initial Rates

- One way to determine values for m and k
- Example: *Decomposition of acetaldehyde*



Rate Law: **Rate = $k[\text{CH}_3\text{CHO}]^m$**

Method:

- Measure *initial rate* for reactions having different $[\text{CH}_3\text{CHO}]$

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Data and Data Crunching

[CH ₃ CHO]	0.10	0.20	0.30	0.40	mol/L
Initial Rate	0.18	0.72	1.6	2.9	mol/L-s

Find Order (m)

For any two data points:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{CH}_3\text{CHO}]_1^m}{k[\text{CH}_3\text{CHO}]_2^m} = \frac{([\text{CH}_3\text{CHO}]_1)^m}{([\text{CH}_3\text{CHO}]_2)^m}$$

$$\frac{0.18}{0.72} = \frac{(0.10/0.20)^m}{1} \quad \Rightarrow \quad 1/4 = (1/2)^m \quad \boxed{m = 2}$$

How does one solve for *m*?

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What about *k* ?

➤ Solve for *k*:

For any data point:

$$\text{Rate} = k[\text{CH}_3\text{CHO}]^2$$

$$k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^2} = \frac{0.18 \text{ mol/L-s}}{(0.10 \text{ mol/L})^2} = \underline{\underline{18. \text{ L/mol-s}}}$$

✓ Knowing *m* and *k*, Rate at *any concentration* can be predicted

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How does Reactant Concentration vary with Time?

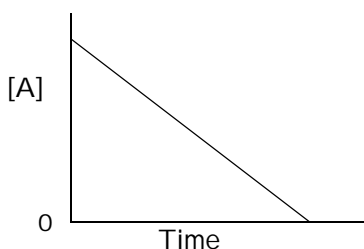
Depends on the reaction *order*:

Integrated Rate Laws

➤ **Zero-th Order Reactions**

- Rate is *independent* of concentration:

$$\text{Rate} = k[A]^0 = k$$



$$[A]_t = -kt + [A]_0$$

slope y-intercept

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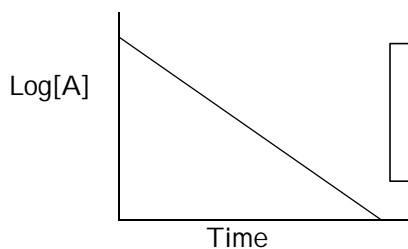
First-Order Reactions

For the reaction: $A \rightarrow \text{products}$

$$\text{Rate} = k[A]^1$$

Using a bit of calculus:

$$\text{Log}[A]_t = -(k/2.303)t + \text{Log}[A]_0$$

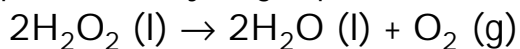


NOTE: Reaction rate *decreases* with time, so that [A] never reaches zero at any finite time t.

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1st-Order Reaction Example

➤ Decomposition of hydrogen peroxide:



$$m=1 \quad k=0.0410 \text{ min}^{-1}$$

If we start with 0.500 mol/L H_2O_2 , what will $[\text{H}_2\text{O}_2]$ be after 10.0 min?

Plug into 1st-order integrated rate equation:

$$\text{Log}[\text{H}_2\text{O}_2]_{10 \text{ min}} = -(0.0410 \text{ min}^{-1}/2.303)(10.0 \text{ min}) + \text{Log}(0.500 \text{ M})$$

$$\text{Log}[\text{H}_2\text{O}_2]_{10 \text{ min}} = -0.479$$

$$[\text{H}_2\text{O}_2]_{10 \text{ min}} = \underline{\underline{0.332 \text{ mol/L}}}$$

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More 1st-Order

How long will it take for $[\text{H}_2\text{O}_2]$ to drop to 0.100 M?

Solve integrated rate law for t :

$$t = (2.303/k)\text{Log}([\text{A}]_0/[\text{A}]_t)$$

Substituting and solving:

$$t = (2.303/0.0410 \text{ min}^{-1}) \text{Log} (0.500/0.100)$$

$$t = \underline{\underline{39.3 \text{ minutes}}}$$

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Special Case

How long will it take for *half* of the H_2O_2 to react?

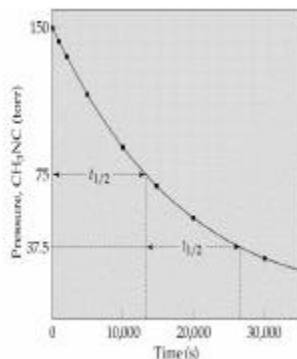
$$t = (2.303/k) \text{Log} (2.00) = \underline{\underline{16.9 \text{ min}}}$$

For *any 1st-order reaction*:

$$t_{1/2} = 0.693/k$$

Half-Life

Time to *halve* the concentration is a *constant!*



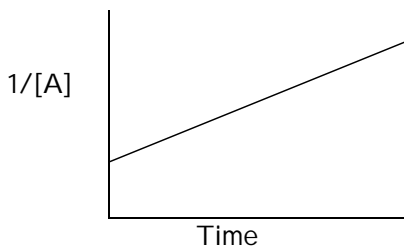
2nd-Order Reactions

For the reaction: $\text{A} \rightarrow \text{products}$

$$\text{Rate} = k[\text{A}]^2$$

Again, with the help of a bit of calculus:

$$1/[\text{A}]_t = kt + 1/[\text{A}]_0$$



Determining m and k

➤ Finding m

Which plot is linear?

$[A]$ vs. t ? → $m = 0$

$\text{Log}[A]$ vs. t ? → $m = 1$

$1/[A]$ vs. t ? → $m = 2$

➤ Finding k

$m = 0$ → $k = -\text{slope}$ ($[A]$ vs. t plot)

$m = 1$ → $k = -2.303 \times \text{slope}$ ($\text{Log}[A]$ vs. t plot)

$m = 2$ → $k = \text{slope}$ ($1/[A]$ vs. t plot)

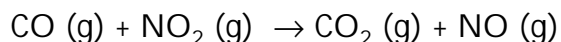
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How do reactions happen?

➤ Collision Theory

Reactions take place as a result of *collisions* between reactants

Example:



$$\text{Rate} = k[\text{CO}][\text{NO}_2]$$

✓ Doubling $[\text{CO}]$ or $[\text{NO}_2]$ will double reaction rate

✓ WHY?

Doubling number of reactant species will double *collision frequency*

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