Kinetics
Rate vs. Time

Created by Schweitzer

02/24/03

Kinetics Mathematics Integrated Rate Law

A ---> products

rate = - (Δ[A]/Δt) = $k[A]^m$

average rate

rate = - (d[A]/dt) = $k[A]^m$

instantaneous rate

Zero Order

- Change in concentration does not effect rate
- Order = 0
- Rate = $k[A]^0$
- Integrated rate law: $[A]_t = -kt + [A]_0$
- Graph = $[A]_t$ vs. t
- Slope = negative (-k)
- Units of k = conc./time

First Order

- Change in concentration is proportional to change in rate
- Order = 1
- Rate = $k[A]^1$
- Integrated rate law: $\ln[A]_t = -kt + \ln[A]_0$
- Graph = $\ln[A]_t$ vs. t
- Slope = negative (-k)
- Units of k = 1/time

Second Order

- Change in rate is proportional to the square of the concentration
- Order = 2
- Rate = $k[A]^2$
- Integrated rate law: $1/[A]_t = kt + 1/[A]_0$
- Graph = $1/[A]_t$ vs. t
- Slope = positive (k)
- Units of k = 1/conc. * time

Integrated rate law summery

Integrated rate laws

Order	Rate	Integrated Rate Equation*	Straight-line Plot	Slope of Plot	Units of k
0	$k[A]^0 = k$	$[A] = -kt + [A]_0$	$[A]$ vs t	$-k$	conc/time
1	$k[A]$	$\ln[A] = -kt + \ln[A]_0$	$\ln[A]$ vs t	$-k$	1/time
2	$k[A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs t	k	1/conc•time

*In this table, $[A]_0$ indicates the initial concentration of substance A, that is, the concentration of A at t = 0, the time when the reaction was started

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What can we do with these equations

- Solve for different concentrations given the time. Order and K must be supplied
- Solve for time at which a concentration will occur Order and K must be supplied
- Determine rate constant (k)
- Determine order of reaction: 0,1,2

Determine Concentration at given time

- The time required for half of a substance to react is 726 seconds. The starting concentration is .600M, what will the concentration be after 1452seconds?

  This reaction is first order.

- What is a ½ life? Can you solve this problem with only half life?

Determine Concentration at given time ANSWER

- Time 0 = [.600]
- 726 sec = [.300]
- **1452 sec = [.150]**

- **Use the equation, determine k?**

Mathematically solve for k

$\ln[A]_t = -kt + \ln[A]_o$

- Rearrange

  $\ln[[A]_t/[A]_o] = -kt$

  $\ln[1/2] = -kt$

  $-.693/-t = k$ (loose negatives)

  Or….. solve for half life (given constant)

  $.693/k = t_{1/2}$

Try this!

- How long will it take the previous experiment to reach a [.100]?

Answer

- K = 9.55E-4 1/s (solved in last problem)
- $\ln[[A_t]/[A]_o = -kt$
  - Insert concentrations and solve for t.
  - T = 1880. seconds

Use graphing to determine order of reaction!

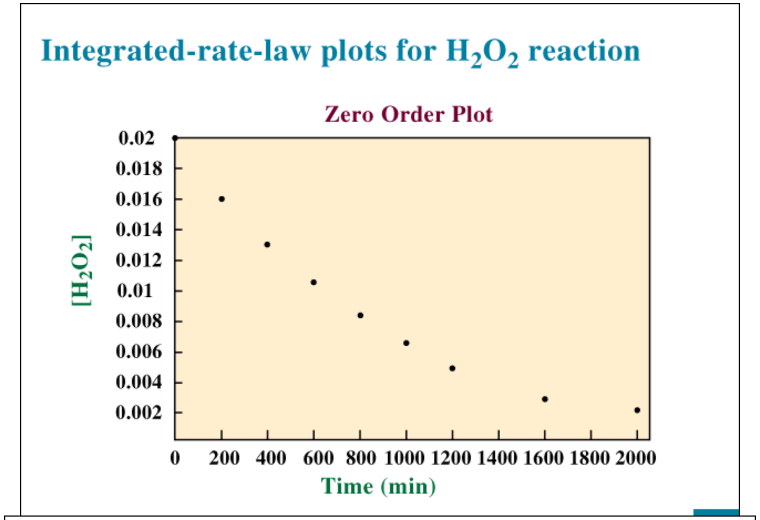
All equations are y = mx +b. If data correctly match up with that equation the line will be straight.

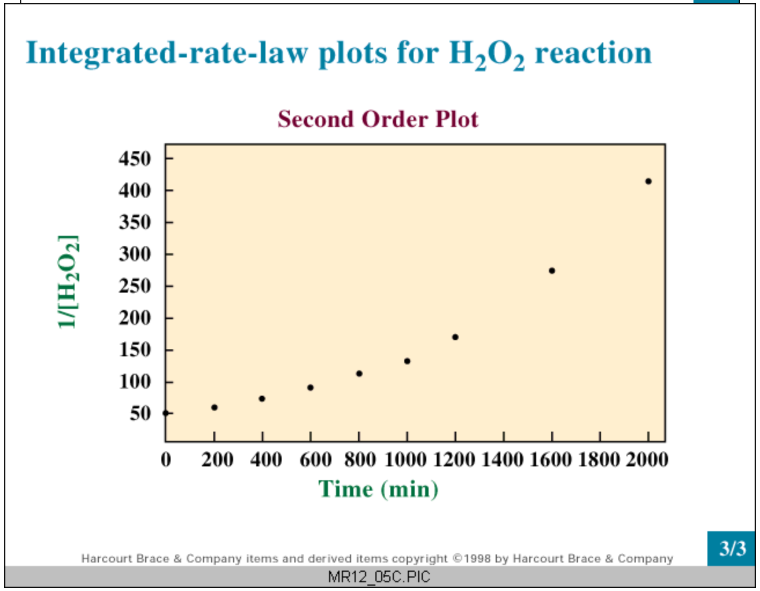
Therefore

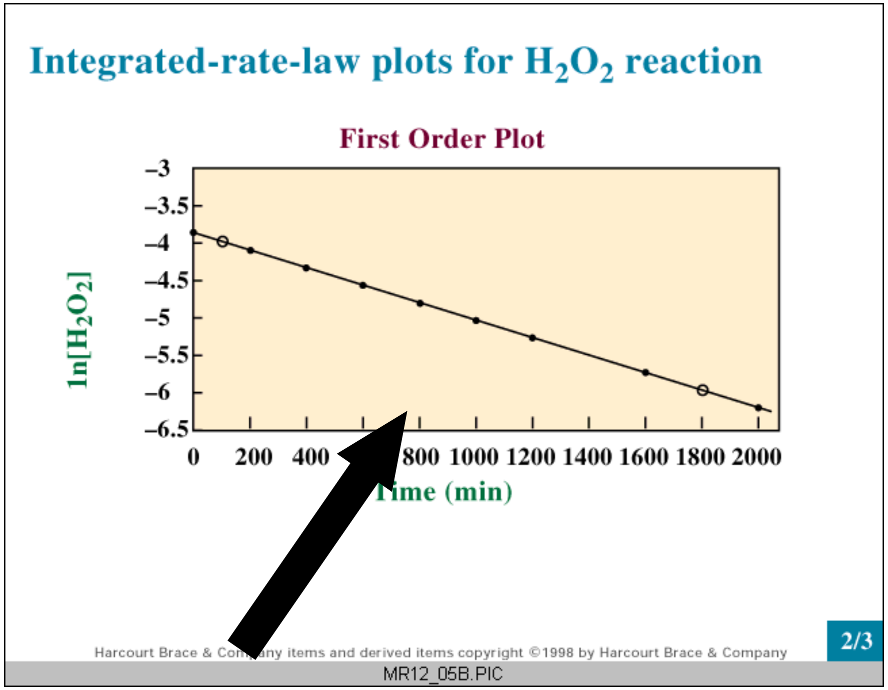
A reaction will only match up with one of the equations

The matched equation is the order

Laboratory example
Goal: Determine order

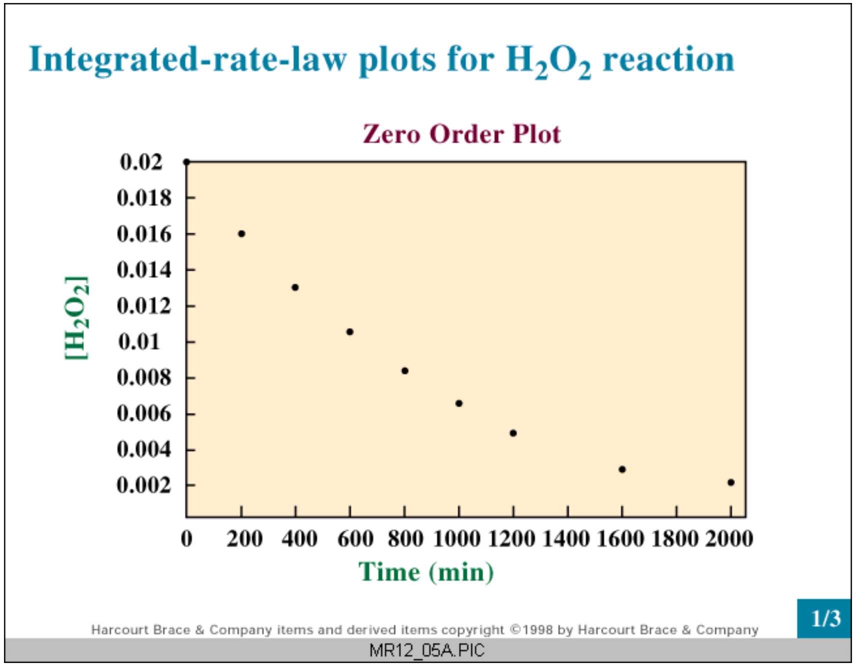






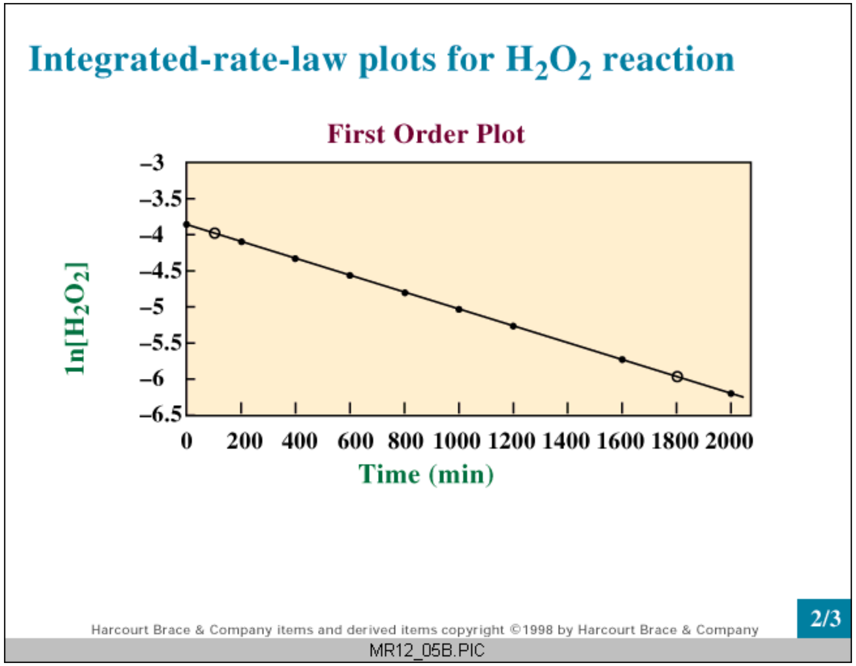
This plot of $\ln[H_2O_2]$ vs. time produces a straight line, suggesting that the reaction is first order.

Is this zero order??



- Notice: as Concentration decreases the rate decreases. If this was zero order the rate would not be affected by the drop in rate.
- note: k = rate (only zero order)
- Note the equation below is a linear y = mx + b equation. In order for this to qualify the graph would have to be straight.
- Not zero order.

Is this reaction 1st order???



Note: $y = mx + b$ is a linear expression
And the graph is straight.

Is this reaction second order

- Y = mx + b is a linear relationship.
- Did the relationship turn out linear?
- No.