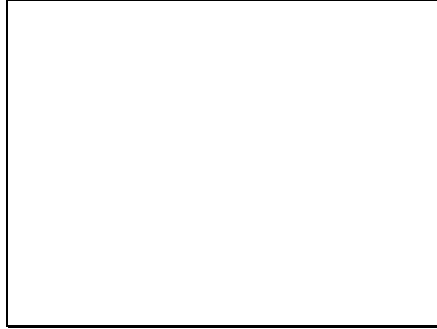


Slide 1



Slide 2

Chapter 13 Problem 47 "Chemistry: A Molecular Approach" by Tro
The data below show the concentration of cyclobutane (C_4H_8) versus time for the following reaction:
 $C_4H_8 \rightarrow 2 C_2H_4$

Determine the order of the reaction and the value of the rate constant.
What is the rate of reaction when $[C_4H_8]=0.25\text{ M}$?

Time (s)	$[C_4H_8]$ (M)
0	1
10	0.894
20	0.799
30	0.714
40	0.638
50	0.571
60	0.51
70	0.456
80	0.408
90	0.364
100	0.326

Slide 3




- Previously, we solved kinetic problems by looking at the initial rates of a reaction when we started with different concentrations of reactants. We then used those initial rates to determine the orders of the reaction and then the rate constant. This problem shows a different way of getting the same information.
-
- Whenever you are monitoring the concentration at different times, you are looking at an "integrated rate law problem". We can still determine the order of the reaction and the rate constant, but it requires looking at the integrated rate law rather than the rate law expression itself.

Slide 4

If you look at the summary in Table 13.2 (pg 587 of Tro), it gives you the relevant information on integrated rate laws. All we need to know is the result, don't worry about how they were determined.

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13.2 Rate Law Summary Table

Rate Law	Units of k	Integrated Rate Law	Straight Line Plot	Half-Life Expression
Rate = $k[A]^0$	$M \cdot s^{-1}$	$[A]_t = -kt + [A]_0$		$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{2} \frac{[A]_0}{k}$
Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$ $\ln \frac{[A]_t}{[A]_0} = -kt$		$t_{1/2} = \frac{0.693}{k} = \frac{1}{k} (0.693)$
Rate = $k[A]^2$	$M^{-1} \cdot s^{-1}$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = -kt$		$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k} \frac{1}{[A]_0}$

Slide 6

What it tells us is that for ALL zero order rate laws, the concentration at any time is a linear function. Specifically, for this reaction, the C_4H_8 concentration at any time is simply the initial concentration minus "kt" (where k is the rate constant and t is the time when the reaction started at t=0 sec). This can be written as:

$$[C_4H_8]_t = [C_4H_8]_0 - kt$$

Where the subscript on the concentration indicates the time: "0" for the initial time=0 sec and "t" for any time after t=0.

It is, possibly, more helpful to look at this equation slightly rearranged:

$$[C_4H_8]_t = -kt + [C_4H_8]_0$$

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In this format, it is more obviously the equation of a straight line ($y=mx+b$, where m is the slope and b is the y -intercept)

$$[C_2H_6]_t = -kt + [C_2H_6]_0$$

$$y = mx + b$$

Now, you can see that a graph of $[C_2H_6]_t$ vs. time should be a straight line with a slope of $-k$ ($m=-k$) and a y -intercept that is the initial concentration ($[C_2H_6]_0$) BUT ONLY IF THE REACTION IS 0 ORDER!

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If the reaction was 1st order, you would have a different integrated rate law:

$$\ln[C_2H_6]_t = \ln[C_2H_6]_0 - kt$$

Again, we can rearrange this to look like a straight line:

$$\ln[C_2H_6]_t = -kt + \ln[C_2H_6]_0$$

$$y = mx + b$$

Now, you can see that a graph of $\ln[C_2H_6]_t$ vs. time should be a straight line with a slope of $-k$ ($m=-k$) and a y -intercept that is the natural log of the initial concentration ($\ln[C_2H_6]_0$) BUT ONLY IF THE REACTION IS 1st ORDER!

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And, similarly, for a 2nd order reaction:

$$\frac{1}{[C_2H_6]_t} = \frac{1}{[C_2H_6]_0} + kt$$

Or:

$$\frac{1}{[C_2H_6]_t} = +kt + \frac{1}{[C_2H_6]_0}$$

$$y = mx + b$$

Now, you can see that a graph of $1/[C_2H_6]_t$ vs. time should be a straight line with a slope of k ($m=k$) and a y -intercept that is the initial concentration ($1/[C_2H_6]_0$) BUT ONLY IF THE REACTION IS 2nd ORDER!

Slide 10

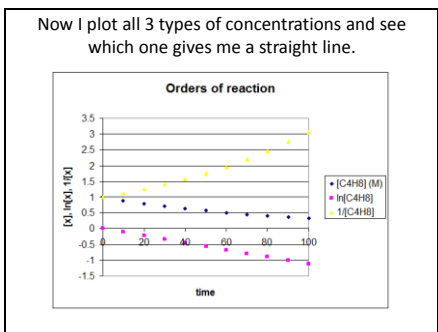
To see how this works in a problem, we can take a couple of approaches:
Graph the data and try to fit it to either a line, a log, or an inverse (1/x) function.
Graph the different forms of the data and see which one is a straight line.

Method 2 is the easiest way to do it and takes about 5 minutes in Excel. I simply add 2 new columns where instead of just the $[C_4H_8]$, I have the ln of the concentration and the inverse.

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Time (s)	[C4H8] (M)	ln[C4H8]	1/[C4H8]
0	1	0	1
10	0.894	-0.11205	1.118568
20	0.799	-0.22439	1.251564
30	0.714	-0.33687	1.40056
40	0.638	-0.44942	1.567398
50	0.571	-0.56037	1.751313
60	0.51	-0.67334	1.960784
70	0.456	-0.78526	2.192982
80	0.408	-0.89649	2.45098
90	0.364	-1.0106	2.747253
100	0.326	-1.12086	3.067485

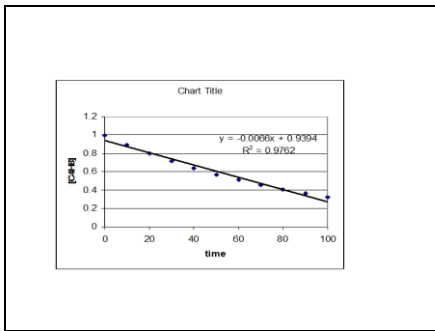
Slide 12



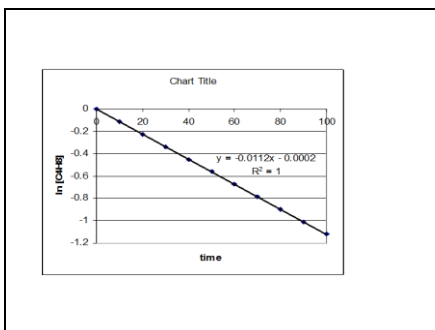
Slide 13

It may not be easy to see, but the ln plot is the straight line. If it helps, plot them on separate curves and add the trendline with the R-squared value. The R-square will tell you if it is a straight line (closer it is to 1.000, the better fit the straight line).

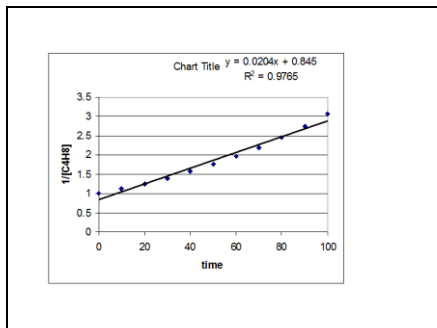
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Slide 15



Slide 16



Slide 17

Since the $\ln[C_4H_8]$ plot gives you a straight line, this means the reaction is 1st order and, best of all, I now know the rate constant, k , since the slope is $-k$:

From the trendline:
 $m = -0.0112$
So, $k = 0.0112 \text{ s}^{-1}$

And we can write the rate law expression:
Rate = $0.0112 \text{ s}^{-1} [C_4H_8]$

I know that seems like a lot of effort, but it really does only take 10 minutes in Excel (or your favorite graphing program). Try one yourself!

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What is the rate of reaction when $[C_4H_8] = 0.25 \text{ M}$?

Once I have the rate law, I can get the rate for any concentration – as long as the temperature is constant:

Rate = $0.0112 \text{ s}^{-1} [C_4H_8]$
Rate = $0.0112 \text{ s}^{-1} [0.25 \text{ M}]$
Rate = $0.0028 \frac{\text{M}}{\text{s}}$

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Integrate rate law vs. rate law

Once I know the order, I have the integrated rate law. For 1st order:

$$\ln \left(\frac{[C_4H_8]_t}{[C_4H_8]_0} \right) = -0.0112t$$

$$\text{Rate} = 0.0112 \text{ s}^{-1} [C_4H_8]$$

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The rate law tells you the rate if you know the concentration.

The integrated rate law tells you the concentration at all times.
