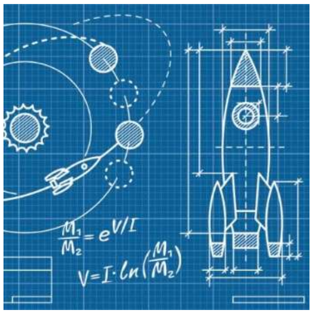
Chapter 13 Chemical Kinetics II

Chapter 13: Chemical Kinetics continued

13.3 Reaction, Concentration, and Time

13.3 Reaction, Concentration, and Time

The Integrated Rate Law Equations are used when time is a factor and allows you to see how the reaction rate changes over time and is used to create a time vs concentration curve.



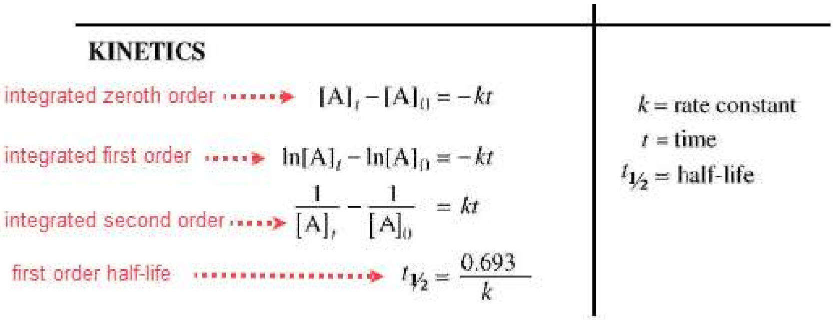
The integrated rate law equations compare two concentrations of a reactant and the time span between them.

$[A]_0$ is the concentration at a specific time in the reaction (usually the start).
$[A]_t$ is the concentration later in the reaction.
k is the same rate constant as found in the instantaneous rate law equation.
t is the time span between $[A]_0$ and $[A]_t$.

The integrated rate law equations differ depending on the order of the reactant.

Order of Reaction	**Instantaneous** Rate law (rate at a given concentration)	**Integrated** Rate Law Concentration changes over time
Zeroth order	rate = $k\,[A]^0$	$[A]_t - [A]_0 = -k \times t$
First order	rate = $k\,[A]^1$	$\ln[A]_t - \ln[A]_0 = -k \times t$
Second order	rate = $k\,[A]^2$	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k \times t$

The 0th, 1st, and 2nd order integrated rate law equations and the half-life equation for 1st order reactions are on the AP Chemistry Equation Sheets.



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integrated zeroth order ······➤ $[A]_t - [A]_0 = -kt$

integrated first order ·····➤ $\ln[A]_t - \ln[A]_0 = -kt$

integrated second order ·····➤ $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

first order half-life ··················➤ $t_{1/2} = \frac{0.693}{k}$

k = rate constant
t = time
$t_{1/2}$ = half-life

Chang covers the integrated rate law equations in 1st order, 2nd order, and 0th order sequence. I will cover the integrated laws in numerical order[1].

Zeroth Order Reactions

Instantaneous rate law: rate = $k\,[A]^0$

Integrated rate law: $[A]_t - [A]_0 = -k \times t$

Zeroth order reactions are unusual since the concentration of the reactant in this type of reaction has no effect on the rate of a reaction. Whether the reactant concentration is 12 *M* or 0.1 *M*, the reaction will progress at the same rate. Thus, for a given temperature, the rate constant will be all that is needed to indicate the speed of the reaction, rate = *k*.

Zeroth order reactions plod along at a constant speed until the reactant is consumed.

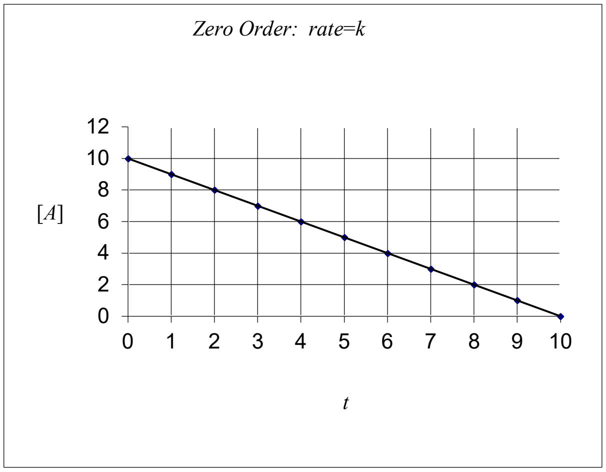
The example in the table below has its concentration drop 1 m*M* each second until [A] = 0.00 m*M*.
Look at the time and [A] table and the resulting graph of concentration vs time.
You should be able to identify this type of reaction order using either the table or the graph.

Zeroth Order Rxn

time *s*	[A] m*M*
0	10.00
1	9.00
2	8.00
3	7.00
4	6.00
5	5.00
6	4.00
7	3.00
8	2.00
9	1.00
10	0.00
100	0.00

Concentration and Time Curve

rate = $k\,[A]^0$



0th order half-life decreases

Zeroth order reactions are rare.

[A] versus *t*

$$k = -\frac{\Delta[A]}{\Delta t}$$

$$k = -\frac{(y_2 - y_1)}{(x_2 - x_1)}$$

$$k = -\frac{(0.00\text{ mM} - 10.00\text{ mM})}{(10.\text{ s} - 0.0\text{ s})}$$

$$k = 1.00\text{ mM s}^{-1}$$

The half-life is the time it takes for the concentration to be halved.
The half-life time from 10.00 m*M* to 5.00 m*M* is 5.0 seconds.
The half-life time from 4.00 m*M* to 2.00 m*M* is 2.0 seconds.
The half-life of a zeroth order reaction decreases with time.

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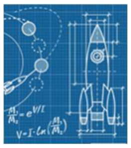
[1] There are other orders of reactions. There are negative and even are fractional orders, but their integrated rate laws will not be covered on the AP Chemistry exam.



First Order Reactions

Instantaneous rate law: rate = k $[A]^1$

Integrated rate law: $\ln[A]_t - \ln[A]_0 = -k \times t$

First order reactions are the most common order, and the math involved has applications in many fields from finance to rocketry.

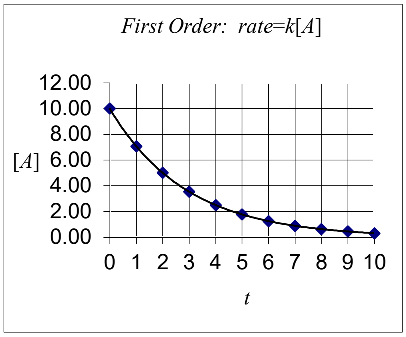
As you would logically expect, the concentration of the reactant can influence the speed of the reaction. This creates a complication in that the reaction rate will change as the reaction progresses. In the first order reaction shown in the table below, the concentration of A drops 3 m*M* in the first second of the reaction, but the drop in concentration between the next second interval is only 2 m*M*. The continuing decrease in rate produces a concentration vs time curve that tapers off approaching 0 m*M* rather than abruptly ending at zero as in the zeroth order reaction. These reactions are best analyzed using a ln [A] versus *t* graph. Since the integrated rate law of the first order reaction uses natural logarithms, you should review your logarithm skills.

First Order Rxn

time *s*	[A] m*M*
0.0	10.00
1.0	7.07
2.0	5.00
3.0	3.54
4.0	2.50
5.0	1.77
6.0	1.25
7.0	0.88
8.0	0.63
9.0	0.44
10.	0.31

Concentration and Time Curve

rate = k [A]



1^{st} order reactions have a constant half-life

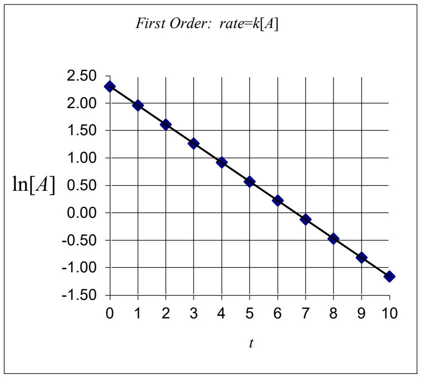
$$k = \frac{0.693}{t_{1/2}}$$

First Order Rxn

time *s*	ln[A]
0.0	2.30
1.0	1.96
2.0	1.61
3.0	1.26
4.0	0.92
5.0	0.57
6.0	0.22
7.0	-0.13
8.0	-0.46
9.0	-0.82
10.	-1.17

Equation to produce a straight line.

ln [A] versus *t*



slope of line: $k = -\frac{\Delta \ln[A]}{\Delta t}$

$$k = -\frac{(y_2 - y_1)}{(x_2 - x_1)}$$

$$k = -\frac{(-1.17 - (2.3))}{(10.\ s - 0.0\ s)} = 0.35\ s^{-1}$$

The half-life time (time for concentration to be cut in half) from 10.00 m*M* to 5.00 m*M* is 2.0 seconds.
The half-life time from 5.00 m*M* to 2.50 m*M* is 2.0 seconds
First order reactions are the only order or reaction that have constant half-lives.
This is a fast, easy way to spot a 1^{st} order reaction.
Using half-lives to solve 1^{st} order reaction rate constants is much easier and faster than calculating the slope of the ln vs time graph. **Most AP questions on 1^{st} order reaction rate problems can be solved quickly using the half-life equation**.

$$k = \frac{0.693}{t_{1/2}} \qquad k = \frac{0.693}{2.0\ \text{s}} = 0.35\ s^{-1}$$

Special note to remember: **Radioactive decay always follows 1^{st} order reaction kinetics**.

Second Order Reactions

Instantaneous rate law: $\text{rate} = k\,[A]^2$

Integrated rate law: $\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = k \times t$

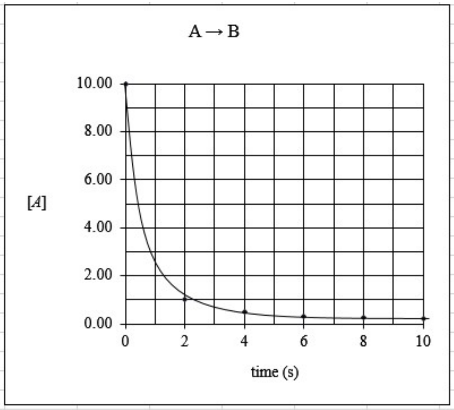
Second order reactions have a tapering curve as the result of the concentration affecting the rate of the reaction. The [A] vs time curve looks much like a 1st order reaction. However, the curve differs in that the half-life is not a constant and instead half-lives increase with time. Also, to plot a straight line, the 1/[A] is plotted against time.
The slope of 1/[A] plotted against time equals the rate constant, *k*.

Second Order Rxn

time *s*	[A] m*M*
0	10.00
1	2.00
2	1.00
3	0.67
4	0.50
5	0.40
6	0.33
7	0.29
8	0.25
9	0.22
10	0.20
100	0.025

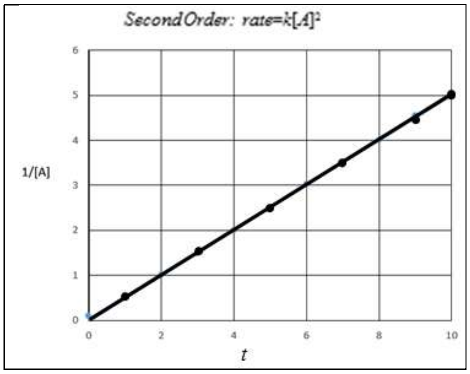
Concentration and Time Curves

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



2nd order reactions have half-lives that increase with time.

Equation to produce a straight line.
1/[A] versus *t*



slope of line: $k = \dfrac{\Delta\left(\dfrac{1}{[A]}\right)}{\Delta t}$

$$k = m = \frac{(y_2 - y_1)}{(x_2 - x_1)}$$

$$k = m = \frac{\left(\frac{1}{0.20\ \text{m}M} - \frac{1}{10.00\ \text{m}M}\right)}{(10.\ \text{s} - 0.0\ \text{s})}$$

$$k = m = \frac{(5.0 - 0.100)\text{m}M^{-1}}{(10. - 0.0\ )\ \text{s}}$$

$$k = 4.9\ \text{mM}^{-1}\ \text{s}^{-1}$$

The half-life time from 1.00 m*M* to 0.50 m*M* is 2.0 seconds.
The half-life time from 0.40 m*M* to 0.20 m*M* is 5.0 seconds.
The half-life of a 2nd order reaction increases with time.

Now that you know about the three orders of reaction, go back, and read about them a second time to get a firm grasp as to how they differ. It is not unusual for there to be 5 points on the exam just on these curves.