

Integrated Rate Laws

Gives the mathematical equation for how reactant concentration varies with time.

A. First Order Reaction: $A \rightarrow \text{Products}$

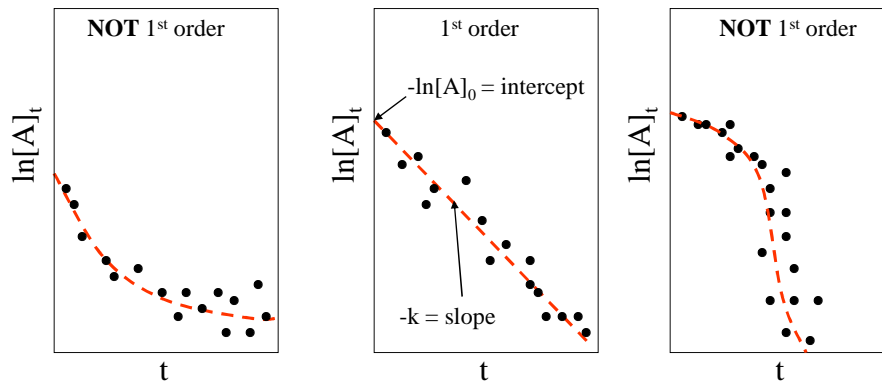
where..... $\text{Rate} = k[A]$ ← This is the equation of the slope
of plot of $[A]$ vs. t

What is the integrated form of this first order rate law??

1. Integrated form of first order rate law which is equation of straight line.....
2. Integrated form of first order rate law in exponential form.....

First Order Rate Law as a Straight Line

$$\ln[A]_t = -k t + \ln[A]_0$$
$$y = mx + b$$



B. Second Order Reaction: $A + A \rightarrow \text{Products}$

where..... $\text{Rate} = k[A]^2$ ← This is the equation of the slope
of plot of [A] vs. t

What is the integrated form of this second order rate law??

1. Integrated form of second order rate law which is equation of straight line.....

C. Zeroth Order Reaction: $A \rightarrow \text{Products}$

where..... $\text{Rate} = k[A]^0$ ← This is the equation of the slope
of plot of [A] vs. t

What is the integrated form of this zeroth order rate law??

1. Integrated form of zeroth order rate law which is equation of straight line.....

Half-Life ($\tau/t_{1/2}$)

Time it takes for half of the original amount of reactant to react/disappear

When one half-life has elapsed...

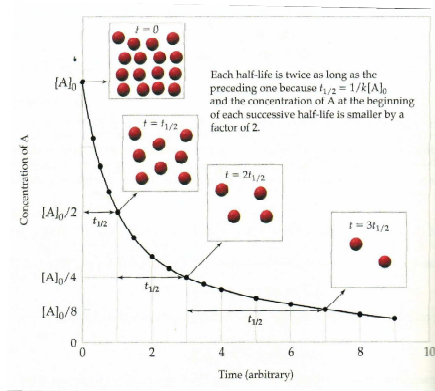
$$t = \tau \text{ or } t_{1/2}$$

and ...

$$[A]_t = \frac{[A]_0}{2}$$

To find the numerical expression for half-life..

Plug the conditions above into the integrated form of the rate law
and rearrange for τ



NOTE: The graph above shows
how the half-life of a second order
Reaction changes with reactant conc.

Half-lives for First, Second, and Zeroth Order Reactions

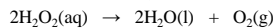
- From the conditions given on the previous slide ($[A]_t = [A]_0/2$ when $t = \tau$), find the equation for the half-life of a first order reaction. For a first order reaction, how does the half-life depend on the initial concentration of reactant?
- From the conditions given on the previous slide ($[A]_t = [A]_0/2$ when $t = \tau$), find the equation for the half-life of a second order reaction. For a second order reaction, how does the half-life depend on the initial concentration of reactant?
- From the conditions given on the previous slide ($[A]_t = [A]_0/2$ when $t = \tau$), find the equation for the half-life of a zeroth order reaction. For a zeroth order reaction, how does the half-life depend on the initial concentration of reactant?

Summary

Kinetics	Integrated Rate Law	Half-life
First Order	$\ln[A]_t = -kt + \ln[A]_0$ OR $[A]_t/[A]_0 = e^{-kt}$	$\tau = \frac{\ln 2}{k}$
Second Order	$1/[A]_t = kt + 1/[A]_0$	$\tau = \frac{1}{[A]_0 k}$
Zeroth Order	$[A]_t = -kt + [A]_0$	$\tau = \frac{[A]_0}{2k}$

Sample Questions

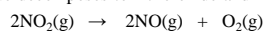
1. The decomposition of hydrogen peroxide in dilute sodium hydroxide solution is described by the equation:



The reaction is first order in H_2O_2 , the specific rate constant for the consumption of H_2O_2 at 20°C is $1.8 \times 10^{-5} \text{ s}^{-1}$, and the initial concentration is 0.30 M .

- What is the half-life (in hours) of the reaction at 20°C ?
 - What is the concentration of H_2O_2 after four half-lives?
 - How many hours will it take for the concentration to drop to 25% of its original value?
 - What will be the concentration of H_2O_2 after 555 minutes?
 - What is the initial rate of the reaction?
2. A reaction is first order in the concentration of reactant. This reaction has a half-life of 102 seconds.
- How much time (in minutes) will it take for 97.0% of the reactant to react?
 - If 0.75 M of reactant is present initially, how much reactant would remain after 2 minutes?
 - After three half-lives what percent of reactant will remain?

3. At elevated temperatures, nitrogen dioxide decomposes to nitric oxide and molecular oxygen:



Concentration-time data for the consumption of NO_2 at 300°C are as follows:

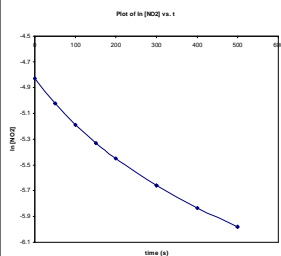
Time (s)	0	50	100	150	200	300	400	500
$[\text{NO}_2]$	8.00×10^{-3}	6.58×10^{-3}	5.59×10^{-3}	4.85×10^{-3}	4.29×10^{-3}	3.48×10^{-3}	2.93×10^{-3}	2.53×10^{-3}

- What is the order of the reaction? (second order in NO_2 , rate = $k[\text{NO}_2]^2$)
- What is the value of the rate constant? ($0.54 \text{ M}^{-1}\text{s}^{-1}$)
- What is the concentration of NO_2 at time $t = 20.0 \text{ min}$? ($1.3 \times 10^{-3} \text{ M}$)
- What is the half-life of the reaction when $[\text{NO}_2]_0 = 6.00 \times 10^{-3} \text{ M}$? ($3.1 \times 10^2 \text{ s}$)
- What is $t_{1/2}$ when $[\text{NO}_2]_0 = 3.00 \times 10^{-3} \text{ M}$? ($6.2 \times 10^2 \text{ s}$)
- How much time will it take for 25 % of NO_2 to react? (77 s)

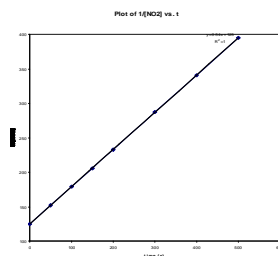
Analysis of Experimental Data

Time (s)	0	50	100	150	200	300	400	500
$[\text{NO}_2]$	8.00×10^{-3}	6.58×10^{-3}	5.59×10^{-3}	4.85×10^{-3}	4.29×10^{-3}	3.48×10^{-3}	2.93×10^{-3}	2.53×10^{-3}
$\ln [\text{NO}_2]$	-4.828	-5.024	-5.187	-5.329	-5.451	-5.661	-5.833	-5.980
$1/[\text{NO}_2]$	125	152	179	206	233	287	341	395

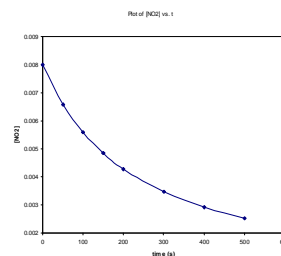
First Order



Second Order



Zero Order



Chem 116
Integrated Forms of Rate Laws

4. The following data were collected for the reaction: $2 \text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ at 580 K

<u>Time (min)</u>	<u>[HI]</u>
0	3.00 M
16.7	0.120 M
33.3	0.061 M
50.0	0.041 M
66.7	0.031 M

- What is the rate law for this reaction?
 - What is the numerical value of the specific rate constant?
 - What is the initial half-life for this reaction?
 - After how much time, will only 20% of the original amount of HI remain?
5. A certain reaction is known to be zeroth order in reactant. Under certain conditions, this reaction has an initial half-life of 16 min at an initial concentration of 0.80 M. How much time will it take for the concentration to drop to 0.05 M?