

9.6: The Method of Half-Lives

Another method for determining the order of a reaction is to examine the behavior of the **half-life** as the reaction progresses. The half-life can be defined as the time it takes for the concentration of a reactant to fall to half of its original value. The method of half-lives involved measuring the half-life's dependence on concentration. The expected behavior can be predicted using the integrated rate laws we derived earlier.

Using the definition of the half-life, at time $t_{1/2}$ the concentration $[A]$ drops to half of its original value, $[A]_0$.

$$[A] = \frac{1}{2}[A]_0$$

at $t = t_{1/2}$.

So if the reaction is 0th order in A , after one half-life

$$\frac{1}{2}[A]_0 = [A]_0 - kt_{1/2}$$

Solving for $t_{1/2}$ reveals the dependence of the half-life on the initial concentration.

$$\frac{[A]_0}{2k} = t_{1/2}$$

So as the original concentration is **decreased**, the half-life of a 0th order reaction will also **decrease**.

Similarly, for a first order reaction,

$$\frac{1}{2}[A]_0 = [A]_0 e^{-kt_{1/2}}$$

and solving for $t_{1/2}$ results in a concentration independent expression

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

It is because the half-life of a 1st order reaction is **independent** of concentration that it is oftentimes used to describe the rate of first order processes (such as radioactive decay.)

For a 2nd order reaction, the half-life can be expressed based on the integrated rate law.

$$\frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$$

solving for $t_{1/2}$ yields

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

In the case of a second order reaction, the half-life **increases** with **decreasing** initial concentration.

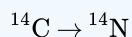
Table 9.6.1: Calculated half lives for Reactions following simple Rate Laws

Order	Half-life	Behavior
0 th	$\frac{1}{2}[A]_0 = [A]_0 - kt_{1/2}$	Decreases as the reaction progresses (as $[A]$ decreases)
1 st	$\left[\frac{\ln 2}{k} = t_{1/2}\right]$	Remains constant as the reaction progresses (is independent of concentration)
2 nd	$\frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$	Increases with decreasing concentration.

For reactions in which the rate law depends on the concentration of more than one species, the half-life can take a much more complex form that may depend on the initial concentrations of multiple reactants, or for that matter, products!

✓ Example 9.6.1: Radiocarbon Dating

Carbon-14 decays into nitrogen-14 with first order kinetics and with a half-life of 5730 years.



What is the rate constant for the decay process? What percentage of carbon-14 will remain after a biological sample has stopped ingesting carbon-14 for 1482 years?

Solution

The rate constant is fairly easy to calculate:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{5730 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

Now the integrated rate law can be used to solve the second part of the problem.

$$[^{14}\text{C}] = [^{14}\text{C}]_o e^{-kt}$$

this can be rewritten in term of relative loss of $[^{14}\text{C}]$.

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_o} = e^{-kt}$$

so

$$\frac{[^{14}\text{C}]}{[^{14}\text{C}]_o} = e^{-(1.21 \times 10^{-4} \text{ yr}^{-1})(1482 \text{ yr})} = 0.836$$

So after 1482 years, there is 83.6 % of ^{14}C still left.

✓ Example 9.6.2:

Based on the following concentration data as a function of time, determine the behavior of the half-life as the reaction progresses. Use this information to determine if the following reaction is 0th order, 1st order, or 2nd order in A. Also, use the data to estimate the rate constant for the reaction.

time (s)	[A] (M)
0	1.200
10	0.800
20	0.600
30	0.480
40	0.400
50	0.343
60	0.300
70	0.267
80	0.240
90	0.218
100	0.200

Solution

If the original concentration is taken as 1.200 M, half of the original concentration is 0.600 M. The reaction takes 20 seconds to reduce the concentration to half of its original value. If the original concentration is taken as 0.800 M, it clearly takes 30 seconds for the concentration to reach half of that value. Based on this methodology, the following table is easy to generate:

$[A]_o$ (M)	1.200	0.800	0.600	0.400
$t_{1/2}$ (s)	20	30	40	60

The rate constant can be calculated using any of these values:

$$k = \frac{1}{[A]t_{1/2}} \quad (9.6.1)$$

$$= \frac{1}{(0.8 \text{ M})(30 \text{ s})} \quad (9.6.2)$$

$$= 0.0417 \text{ M}^{-1} \text{ s}^{-1} \quad (9.6.3)$$

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