

A Brief Summary of Rate Laws

Reminder: there are 2 types of rate laws!

- ❖ **Differential rate law:** data table contains Concentration and rate data. Compare change in rate when one reactant is held constant but another doubles to determine the order of the reactants and the value of the rate constant, k .
- ❖ **Integrated rate law:** data table contains concentration and time data. (BE CAREFUL: the Tro textbook calls this the 'differential rate law'!!) Use graphical methods determine the order of a given reactant and the value of the rate constant k .

Integrated Rate Laws Review: set time as your x-axis, and graph three different y-axes (in alphabetical order!)

Order	Rate Law	Linear Plot	Straight Line Equation	Half-life
0 th	Rate = $k[A]^0 = k$	Concentration, $[A]$ vs time	$[A]_t - [A]_0 = -kt$	totally exists. (but not AP tested)
1 st	Rate = $k[A]^1$	Natural log, $\ln[A]$ vs time	$\ln[A]_t - \ln[A]_0 = -kt$	$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$ <small>on F.C.</small>
2 nd	Rate = $k[A]^2$	Reciprocal, $1/[A]$ vs time	$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$	totally exists. (but not AP tested)

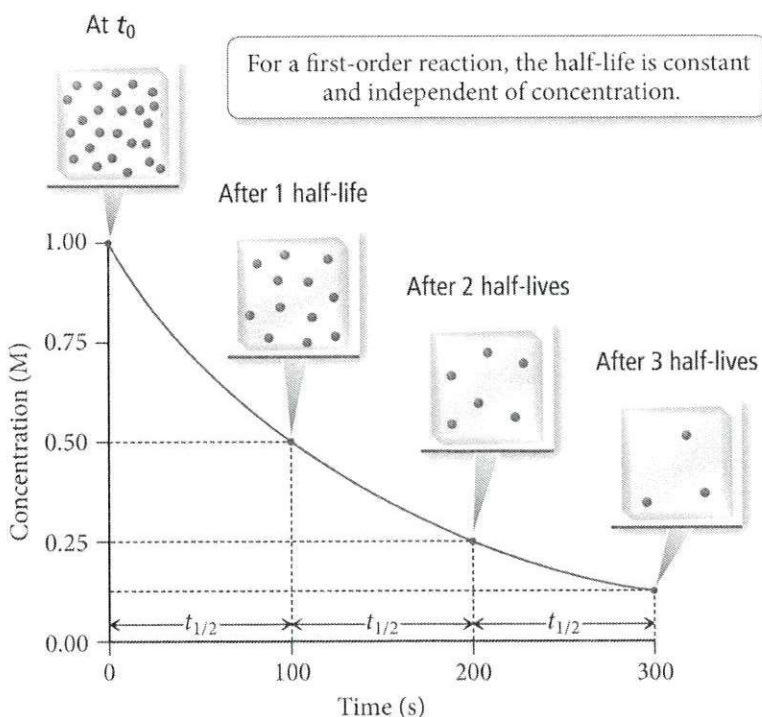
Half-life ($t_{1/2}$): time required for 50% of the original reactant sample to disappear. get used up

- The AP test focuses on the half-life of 1st order reactions only!! They are the only types of reactions for which the length of a half-life is constant. ← only changes if temp. changes, NOT [reactants]

In a first order reaction, the half-life equation is as follows:

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \quad \text{on F.C.}$$

Half-Life for a First-Order Reaction



Let's Practice!

1. A certain first order reaction has a half-life of 20.0 minutes.

a. Calculate the rate constant for this reaction.

$$t_{1/2} = \frac{0.693}{k} = 20.0 \text{ min} \Rightarrow k = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

b. How much time is required for this reaction to be 75% complete?

100% $\xrightarrow{t_{1/2}}$ 50% $\xrightarrow{2 \cdot t_{1/2}}$ 25% left = 75% complete

$$2 \cdot t_{1/2} = 2(20.0 \text{ min}) = 40.0 \text{ min}$$

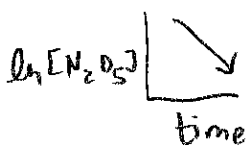
2. Dinitrogen pentoxide decomposes according to the equation $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$

The following data were collected for this reaction at a given temperature:

^{0th} [N ₂ O ₅]	^{1st} ln[N ₂ O ₅]	^{2nd} 1/[N ₂ O ₅]	Time (sec)
1.00	0.00	1.00	0
0.82 } 0.18	-0.20 } 0.20	1.22 } 0.22	25
0.68 } 0.14	-0.39 } 0.19	1.48 } 0.26	50
0.56 } 0.12	-0.59 } 0.20	1.80 } 0.32	75
0.46	-0.78 } 0.19	2.18	100
0.38	-0.98	2.65	125
0.31	-1.17	3.23	150

t_{1/2} is indicated between 75 and 100 seconds.

a) What is the order of this reaction? Write the rate law expression. Justify your answer (you may include a sketch of a graph as part of your explanation). 1st order w/ respect to N₂O₅, b/c a plot of ln [N₂O₅] vs. time will be linear w/ a negative slope (as shown by the approximately constant rate of change in ln [N₂O₅] every 25 sec).



b) Determine the value of the rate constant for this reaction (including units).

$$k = |\text{slope}| = \left| \frac{\Delta y}{\Delta x} \right| = \left| \frac{\Delta \ln [\text{N}_2\text{O}_5]}{\Delta \text{time}} \right| = \left| \frac{-0.20 - 0}{25 - 0} \right| = \frac{0.20}{25} = 0.0080 \text{ s}^{-1}$$

c) Determine the half-life for the reaction under the conditions of this experiment.

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0080} = 87 \text{ s} \quad \text{* matches data!}$$