Example: The method of initial rates was used to study the reaction

$$BrO_3^-(aq) + 5\,Br^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(l)$$

The following data were collected.

Expt	$[BrO_3^-]$	$[Br^-]$	$[H^+]$	Initial Rate of consumption of BrO_3^-
1	$0.10\ \frac{mol}{L}$	$0.10\ \frac{mol}{L}$	$0.10\ \frac{mol}{L}$	$8.0\times10^{-4}\ \frac{mol\ L^{-1}}{s}$
2	0.15	0.10	0.10	1.2×10^{-3}
3	0.15	0.15	0.10	1.8×10^{-3}
4	0.15	0.10	0.20	4.8×10^{-3}

(a) Use the data to deduce the rate law and the value of the rate constant.

(b) What are the initial rates of consumption of Br^- and H^+ if the initial concentrations are $[BrO_3^-] = 0.25\ \frac{mol}{L}$, $[Br^-] = 0.15\ \frac{mol}{L}$ and $[H^+] = 0.20\ \frac{mol}{L}$?

Example: The chemical equation describing the conversion of cyclobutane (C_4H_8) to ethene (C_2H_4) is

$$C_4H_8(g) \rightarrow 2\ C_2H_4(g).$$

The reaction is first-order with respect to C_4H_8 and the rate constant is k = 0.0277 min^{-1} at 449^oC. If 0.400 mol of C_4H_8 is placed in a 1.00-L reaction vessel at 449^oC, then how long will it take for 25% of the cyclobutane to react?

Example: Suppose that the reaction A $\rightarrow$ products is second-order with k = 0.0277 mol^{-1} L min^{-1}. How long will it take for [A] to decrease from 0.400 mol L^{-1} to 0.300 mol L^{-1} ?

Example: Use the algebraic approach, together with the data below, to determine whether the reaction

$$2\ NOCl(g) \rightarrow 2\ NO(g) + Cl_2(g)$$

is zeroth-, first- or second-order. What is the rate constant, *k*?

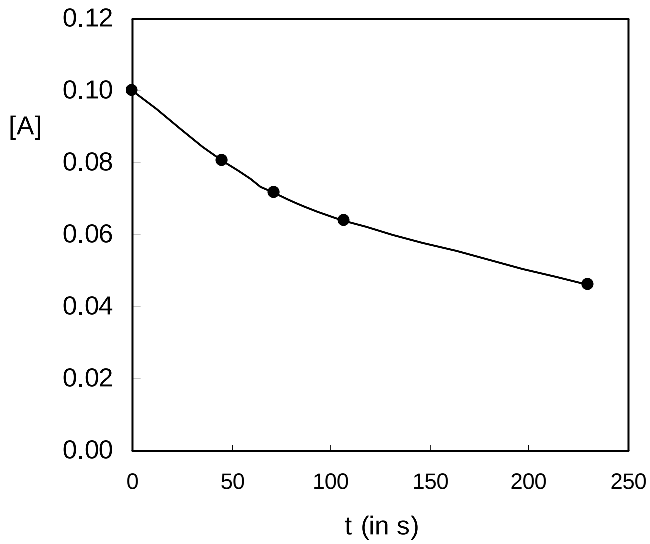
***t* (in s)**	**[NOCl] (in $\frac{mol}{L}$)**			
0	0.100			
30	0.064			
60	0.047			
200	0.021			

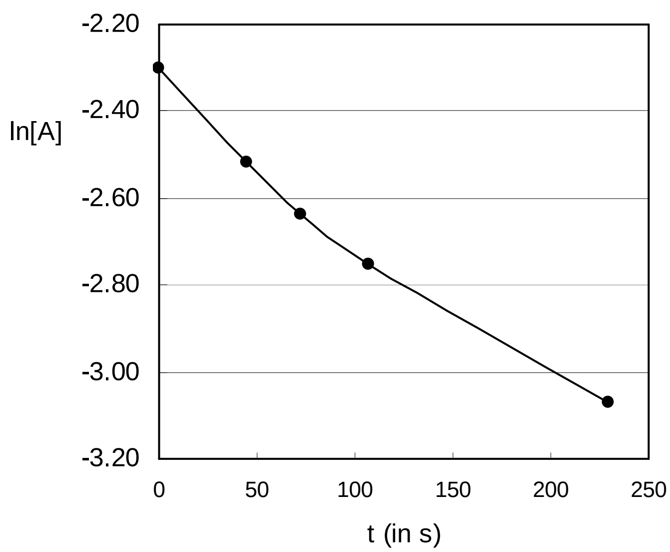
Example: Use the graphical approach, together with the data below, to determine whether the reaction

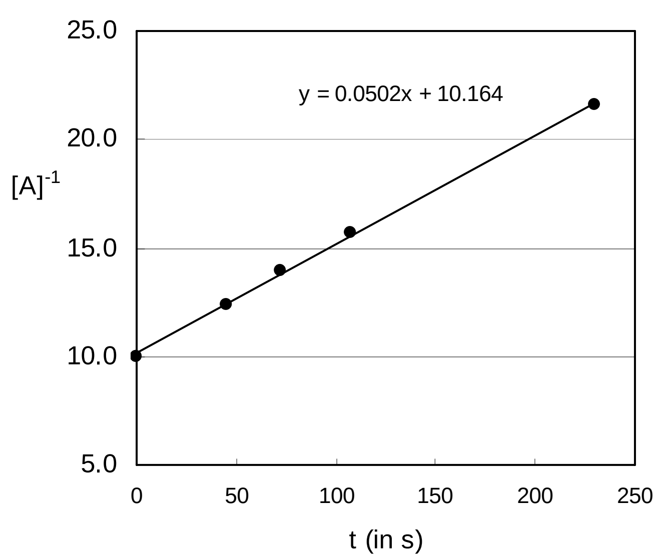
$$NH_4CNO(aq) \rightarrow (NH_2)_2CO(aq)$$

is zeroth-, first- or second-order. What is the rate constant, *k*?

***t* (in min)**	**[NH_4CNO] (in $\frac{mol}{L}$)**		
0.0	0.1000		
45.0	0.0808		
72.0	0.0716		
107.0	0.0638		
230.0	0.0463		


0.12
0.10
0.08
0.06
0.04
0.02
0.00
[A]
0
50
100
150
200
250
t (in s)


-2.20
-2.40
-2.60
-2.80
-3.00
-3.20
ln[A]
0
50
100
150
200
250
t (in s)


25.0
20.0
15.0
10.0
5.0
[A]-1
y = 0.0502x + 10.164
0
50
100
150
200
250
t (in s)

Example: Nuclear decay is a first-order process. The chemical equation describing the nuclear decay of carbon-14 is:

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + e^{-}.$$

The half-life of carbon-14 is 5730 years. If an ancient artifact contains only 10% as much carbon-14 as a living object, what is the age of the artifact?

Did you know?
All living things, both plant and animal, maintain small, but constant, levels of ^{14}C. When a plant is harvested, or when an animal dies, the amount of ^{14}C decreases slowly with time.

Example: Consider the mechanism below and find the rate law for the overall reaction.

Step 1: $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ fast

Step 2: $O_3 + O \xrightarrow{k_2} 2\,O_2$ slow

Overall: $2\,O_3 \longrightarrow 3\,O_2$

Example: Use the mechanism below to deduce the rate law for the overall reaction.

$$Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Br \qquad \text{(fast)}$$

$$2\,Br + H_2 \xrightarrow{k_2} 2\,HBr \qquad \text{(slow)}$$

$$Br_2 + H_2 \rightarrow 2\,HBr$$

Example: Consider the mechanism below and find the rate law for the overall reaction.

Step 1: $NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + Cl$

Step 2: $NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$

Overall: $2\ NO_2Cl \longrightarrow 2\ NO_2 + Cl_2$

Example: In the previous example, we saw that the rate law was:

$$Rate = \frac{k_1 k_2 [NO_2Cl]^2}{k_{-1}[NO_2] + k_2[NO_2Cl]}$$

Show that the rate law is first-order with respect to NO_2Cl when $[NO_2Cl]$ is large and second-order with respect to NO_2Cl when $[NO_2Cl]$ is small.

Example: Consider the mechanism given in the second previous example. Write down an expression for the net rate of consumption of NO_2Cl. Then use the steady-state approximation to show that you obtain a result which is consistent with the result we obtained previously.

This example is meant to illustrate that it doesn't matter which reactant or product you choose to follow. You get the same final result..

Example: Consider the reaction $C_2H_5I + OH^- \rightarrow C_2H_5OH + I^-$.

The rate constant has the following values:

$k = 5.03 \times 10^{-2}$ $(mol/L)^{-1}$ s^{-1} at 289 K

$k = 6.71$ $(mol/L)^{-1}$ s^{-1} at 333 K

What is E_a for the reaction? By what factor does the rate of reaction increase if T is increased from 289 K to 300 K?

<u>Example</u>: The activation energies for the catalyzed and uncatalyzed decompositions of $H_2O_2(aq)$ are 56.5 kJ mol^{-1} and 75.3 kJ mol^{-1}, respectively. By what factor does the rate increase if a catalyst is used? Assume T = 298 K. Assume that the rate constants obey the Arrhenius equation and that pre-exponential factors are equal.