Kinetics: Obtaining a Rate Law from Experimental Data

1. Question: Determine the rate law and rate constant for the following reaction at 450 K using the data in the table provided.

$$X + 2Y \rightarrow Z$$

Initial rate of the reaction at 450 K (M/s)	[X], M	[Y], M
0.0016	0.01	0.01
0.0048	0.01	0.03
0.0192	0.02	0.03
0.1024	0.04	0.04

Answer: The generic form for the rate law is:

Rate = $k[X]^x[Y]^y$. The powers, x and y, are determined from the experimental data and NOT from the coefficients of the equation.

To determine x, find two experiments where [Y] is held constant. The 2nd and 3rd sets of data meet that criteria. Set up a ratio of rates and concentrations as follows:

$$\frac{\text{rate}_{exp3}}{\text{rate}_{exp2}} = \frac{0.0192}{0.0048} = 4 \qquad \frac{[X]_{exp3}}{[X]_{exp2}} = \frac{0.02}{0.01} = 2$$

Now ask the question, "What power would I have to raise the concentration by, that is, 2; to get the observed effect on rate, that is, 4.

$2^x = 4$, x = 2. The reaction is second-order in X.

To determine y, find two experiments where [X] is held constant. The 1st and 2nd sets of data meet that criteria. Set up a ratio of rates and concentrations as follows:

$$\frac{\text{rate}_{exp2}}{\text{rate}_{exp1}} = \frac{0.0048}{0.0016} = 3 \qquad \frac{[X]_{exp2}}{[X]_{exp1}} = \frac{0.03}{0.01} = 3$$

Now ask the question, "What power would I have to raise the concentration by, that is 3, to get the observed effect on rate, that is 3.

$3^y = 3$, y = 1. The reaction is first-order in Y.

This gives a rate law of

$$\text{Rate} = k[X]^2[Y]$$

To determine the rate constant at this temperature, take a set of experimental data, plug in the values, and solve for k. In this solution, the first set of experimental data is used.
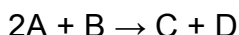
$$\text{Rate} = k[X]^2[Y]$$

$$0.0016 \text{ M/s} = k[0.01 \text{ M}][0.01 \text{ M}]^2$$

$$0.0016 \text{ M/s} = k(0.000001 \text{ M}^3)$$

$$1.6 \times 10^3 \text{ s}^{-1}\text{M}^{-2} = k$$

The best value for k would be obtained by performing the above calculation for each set of experimental data and averaging the values together.

2. Question: Determine the rate law for the following reaction at 250°C using the data in the table provided.

$$2A + B \rightarrow C + D$$

Initial rate of the reaction at 250°C, M/s	[A], M	[B], M
0.0037	0.12	1.8
0.0148	0.12	3.6
0.0617	0.24	5.2
0.1732	0.49	6.1

Answer: Compared to the previous problem, this problem has a complicating fact. There is no experimental results for holding [B] constant.

The rate law will have the generic form Rate = $k[A]^x[B]^y$. Begin by determining the order of B (that is, determining the value of y). To do this, we will select experiments 1 and 2 because these two hold [A] constant. See that the effect the change in [B] has on the rate.

$$\frac{rate_{exp2}}{rate_{exp1}} = \frac{0.0148}{0.0037} = 4 \qquad \frac{[B]_{exp2}}{[B]_{exp1}} = \frac{3.6}{1.8} = 2$$

What power would the concentration of 2 need to be raised to in order to produce a change in rate of 4? $2^y = 4$, $y = 2$. The reaction is 2nd order in B.

To determine A, we would like to find an experiment where B is held constant. There is not one. Take the rate law, with the known order and solve for the substance for which you do not know the order:

$$rate = k[A]^x[B]^2$$

$$\frac{\text{rate}}{k[\text{B}]^2} = [\text{A}]^x$$

Now, take two experiments (experiments 2 and 3 are demonstrated here) and see how a change in concentration of A affects the quantity on the left side of the equation. (Note: units were removed for ease in following the solution.)

$$\frac{\dfrac{0.0617}{k(5.2)^2}}{\dfrac{0.0148}{k(3.6)^2}} = \left(\frac{0.24}{0.12}\right)^x$$

$$2 = 2^x$$

Therefore x = 1 and it is first-order in A.

The rate law is therefore: Rate = $k[\text{A}][\text{B}]^2$

Kinetics: First-Order Kinetics and the Integrated Rate Law

1. Question: Consider the data collected for the reaction

A → products

[A], M	Time, s
0.74	20
0.64	30
0.47	50
0.38	65

Determine the order for the reaction.

Answer: The most common order for a reactant is first order. When given concentration and time information for a reaction, begin by plotting ln[A] versus t. If this produces a linear graph, the reaction is first-order. If not, the reaction is not first-order. Then a plot of 1/[A] v. t can be produced to see if the reaction is second-order.

Take the natural log of each of the concentration values.
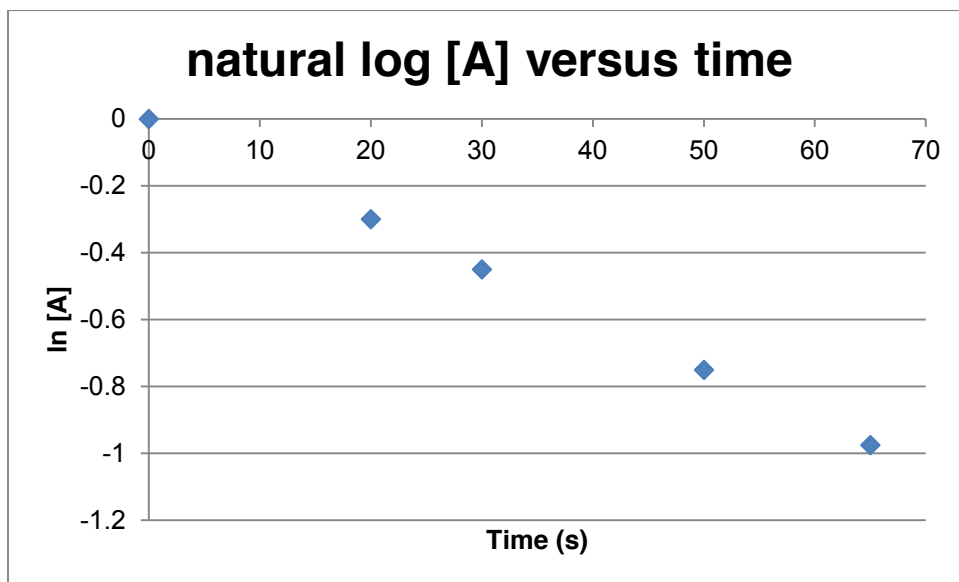
The reaction is first-order.

2. Question: The rate constant of a certain first-order reaction is 5.24×10^{-3} s^{-1}. The reaction starts with a concentration of reactant of 0.250 M. What is the concentration of the reactant after 1.50 minutes?

Answer: The first-order integrated rate law equation is:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

According to the wording of the problem, $[A]_0 = 0.250$ M. The rate constant, k, is in units of s^{-1} therefore, the time needs to be in seconds as well:

$$t = 1.50 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} = 90.0 \text{ s}$$

Plug the values given into the rate law and solve for $[A]_t$, the concentration of the reactant at time of 90.0 seconds.

$$\ln \frac{[A]_t}{0.250 \text{ M}} = -(5.24 \times 10^{-3} \text{ 1/s}) \times (90.0 \text{ s})$$

$$\ln \frac{[A]_t}{0.250 \text{ M}} = -0.472$$

$$\frac{[A]_t}{0.250 \text{ M}} = e^{(-0.472)}$$

$$\frac{[A]_t}{0.250 \text{ M}} = 0.624$$

$$[A]_t = (0.624) \times (0.250 \text{ M}) = 0.156 \text{ M}$$

Kinetics: First-Order Kinetics and Half-Life

1. Question: The half-life for the first-order conversion of cyclopropane to propene at 773 K is 17 min. What is the rate constant (in units of s^{-1}) for the reaction at the same temperature?

   Answer: For a first-order reaction the relationship between half-life and the rate constant is given by:

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

Watch carefully the units. The half-life time is given in minutes and the units of s^{-1} are needed for k. Convert time to seconds:

$$t_{1/2} = 17 \text{ min} \times \frac{60 \text{ s}}{1 \text{min}} = 1020 \text{ s}$$

Solve the half-life equation for k:

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

Plug in the value for half-life gives:

$$k = \frac{0.693}{1020 \text{ s}} = 6.8 \times 10^{-4} \text{ s}^{-1}$$

2. The half-life for the first-order conversion of cyclopropane to propene at 773 K is 17 min. Determine the amount of time required (in min) to convert 30% of the cyclopropane to propene.

Answer: Using the rate constant, k, obtained in the previous question, the amount of time required to decrease the reactant from 100% down to 70% (30% reacted) can be determined using the first-order integrated rate law as follows:

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{70\%}{100\%} = -(6.8 \times 10^{-4} \text{ s}^{-1}) \times t$$

$$-0.357 = -(6.8 \times 10^{-4} \text{ s}^{-1}) \times t$$

$$\frac{-0.357}{6.8 \times 10^{-4} \text{ s}^{-1}} = t = 525 \text{ s}$$

Now, convert the time to minutes:

$$t = 525 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 8.7 \text{ min}$$

Note: The problem could have been worked by determining the rate constant in min^{-1}, instead of caring the rate constant forward (in s^{-1}) from the previous problem.

3. A certain first-order reaction required 456 s to reduce the amount of reactant to 1/16 of its original concentration at 450 K. What is the half-life of the reaction at this temperature?

Answer: The reduction to 1/16 of the original amount is 4 half-lives. (1/2, 1/4, 1/8, 1/16). The total time is 456 s. Dividing this time by 4 will give the time for 1 half-life.

$$\frac{456 \text{ s}}{4} = 114 \text{ s}$$