

Kinetics: The Differential and Integrated Rate Laws in Chemistry (and Physics, Biology, etc.)

In general, for all reactions: $aA \rightarrow bB + cC$

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt}$$

*Notice for the reactants, there is a negative sign in front. This is because as time progresses, the concentration of reactant decreases. For products, their concentration over time increases which is why theirs is positive (no negative sign in front).

As reactant A goes to product B: $A \rightarrow B$

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n$$

*In the following derivations of the three integrated rate laws, we assume the stoichiometric coefficient "a" in front of reactant A is 1.

1st order reaction

Differential Rate Law

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^1$$

Separate the variables

$$\frac{d[A]}{[A]} = -k dt$$

Integrate both sides of the equation

$$\int \frac{d[A]}{[A]} = \int -k dt = -k \int dt$$

Indefinite integral constant, b

$$\ln[A] = -kt + b$$

At time $t = 0$, $b = \ln[A]_0$ where $[A]_0$ is the initial reactant concentration

Integrated Rate Law (linear form)

$$\ln[A] = -kt + \ln[A]_0$$

To more clearly see the exponential relationship between time, t , and reactant concentration, $[A]$, for a first-order reaction we can convert the integrated first-order rate-law (linear form) to its non-linear exponential form:

Integrated Rate Law (linear form) $\ln[A] = -kt + \ln[A]_0$

Raise both sides to the power of e $e^{\ln[A]} = e^{-kt} e^{\ln[A]_0}$

Simplify, and obtain non-linear form $[A] = [A]_0 e^{-kt}$

One can also then write the non-linear differential rate law:

$$\text{Rate} = \frac{-d[A]}{dt} = k[A] = k[A]_0 e^{-kt}$$

2nd order reaction

Differential Rate Law

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^2$$

Separate the variables

$$\frac{-d[A]}{[A]^2} = k dt$$

Integrate both sides of the equation

$$\int -\frac{d[A]}{[A]^2} = \int k dt = k \int dt$$

Indefinite integral constant, b

$$-\left(-\frac{1}{[A]}\right) = kt + b$$

At time $t = 0$, $b = \left(\frac{1}{[A]_0}\right)$ where $[A]_0$ is the initial reactant concentration

Integrated Rate Law

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Zero-order reaction

Differential Rate Law

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^0$$

Simplify

$$\frac{-d[A]}{dt} = k$$

Separate the variables

$$d[A] = -kdt$$

Integrate both sides of the equation

$$\int d[A] = \int -k dt = -k \int dt$$

Indefinite integral constant, b

$$[A] = -kt + b$$

At time $t = 0$, $b = [A]_0$ where $[A]_0$ is the initial reactant concentration

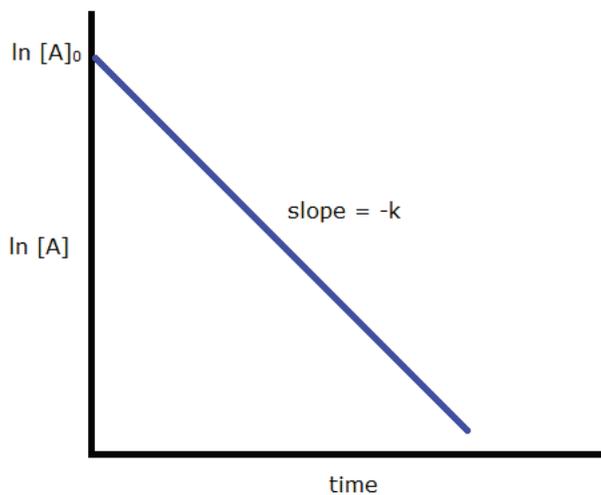
Integrated Rate Law

$$[A] = -kt + [A]_0$$

First, Second, and Zero Order Plots for Chemical Reactions

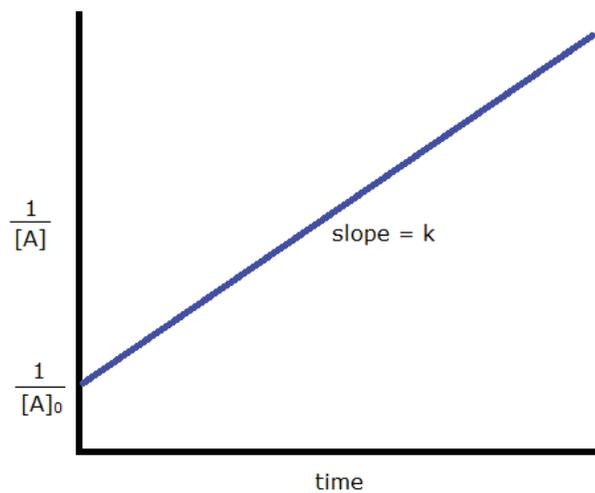
1st order reaction

$$\ln[A] = -kt + \ln[A]_0$$



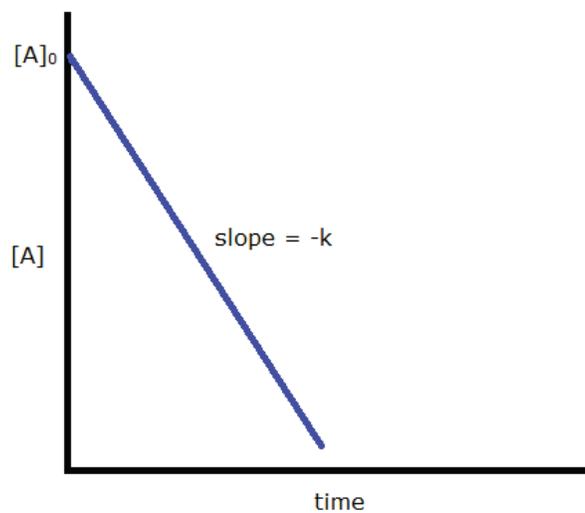
2nd order reaction

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$



Zero-order reaction

$$[A] = -kt + [A]_0$$



Integrated Rate Law (continued)

- As reactant A goes to product B: $aA \rightarrow bB$

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n$$

*In the following derivations of the three integrated rate laws, we assume the stoichiometric coefficient "a" in front of reactant A is no longer 1.

- Therefore, with each new integrated rate law, the proportionality constant is now written as **ak'**. However, when a rate constant is given, we treat it as a generic proportionality constant and call it k. This is because when an experiment is first performed in lab, the overall balanced reaction with correct coefficients is unknown. To figure out the order of the reaction, the data points are plotted and the slope is calculated and just called **k**.

1st order reaction: $2A \rightarrow B$

Differential Rate Law

$$\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = k[A]^1$$

Separate the variables

$$\frac{d[A]}{[A]} = -2k dt$$

Integrate both sides of the equation

$$\int \frac{d[A]}{[A]} = \int -2k dt = -2k \int dt$$

Indefinite integral constant, b

$$\ln[A] = -2kt + b$$

At time $t = 0$, $b = \ln[A]_0$ where $[A]_0$ is the initial reactant concentration

Integrated Rate Law (linear form)

$$\ln[A] = -2k't + \ln[A]_0$$

2nd order reaction: $3A \rightarrow B$

Differential Rate Law	$\text{Rate} = -\frac{1}{3} \frac{d[A]}{dt} = k[A]^2$
Separate the variables	$\frac{d[A]}{[A]^2} = -3k dt$
Integrate both sides of the equation	$\int -\frac{d[A]}{[A]^2} = \int 3k dt = 3k \int dt$
Indefinite integral constant, b	$-\left(-\frac{1}{[A]}\right) = 3kt + b$
At time $t = 0$, $b = \left(\frac{1}{[A]_0}\right)$ where $[A]_0$ is the initial reactant concentration	
Integrated Rate Law	$\frac{1}{[A]} = 3k't + \frac{1}{[A]_0}$

Zero-order reaction: $4A \rightarrow B$

Differential Rate Law	$\text{Rate} = -\frac{1}{4} \frac{d[A]}{dt} = k[A]^0$
Simplify	$-\frac{1}{4} \frac{d[A]}{dt} = k$
Separate the variables	$d[A] = -4kt$
Integrate both sides of the equation	$\int d[A] = \int -4k dt = -4k \int dt$
Indefinite integral constant, b	$[A] = -4kt + b$
At time $t = 0$, $b = [A]_0$ where $[A]_0$ is the initial reactant concentration	
Integrated Rate Law	$[A] = -4k't + [A]_0$

Half-Life

- The half-life of a reaction ($t_{1/2}$) is defined as the time it takes for the concentration of the reactant to decrease to half its original concentration.

-The shorter the half-life, the faster the reaction...the faster the reaction, the larger the rate constant.

1st order reaction

Integrated Rate Law

$$\ln[A] = -kt + \ln[A]_0$$

At time $t = t_{1/2}$

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

Substitute for $[A]$

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

Rearrange the terms

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

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

$$-0.693 = -kt_{1/2}$$

Half-life equation

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

2nd order reaction

Integrated Rate Law

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

At time $t = t_{1/2}$

$$[A] = \frac{1}{2} [A]_0 \quad \text{Therefore} \quad \frac{1}{[A]} = 2 \cdot \frac{1}{[A]_0}$$

Substitute for $[A]$

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

Rearrange the terms

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

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

Half-life equation

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

*Note that the half-life for a 2nd order reaction depends on the initial concentration of reactant; it is inversely proportional. Thus, the larger the initial concentration, the smaller the half-life.

Zero-order reaction

Integrated Rate Law

$$[A] = -kt + [A]_0$$

At time $t = t_{1/2}$

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

Substitute for $[A]$

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

Rearrange the terms

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

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

Half-life equation

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

*Note that the half-life for a zero-order reaction depends on the initial concentration of reactant; it is directly proportional. Thus, the larger the initial concentration, the larger the half-life.

Examples Using Integrated Rate Laws and Half-Lives in Chemistry

1st order reaction



- Write the overall rate expression for this first order reaction.

$$\text{rate} = k[\text{N}_2\text{O}_5]^1$$

*Note that the exponent does not match the coefficient in front of N_2O_5 . By just looking at the overall balanced equation, you cannot tell the order of the reaction.

- The half-life of N_2O_5 at 25°C is 1.87×10^4 seconds. Determine the rate constant for the above reaction.

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

$$1.87 \times 10^4 = \frac{0.693}{k}$$

$$k = 3.7 \times 10^{-5} \text{ s}^{-1}$$

- Using the information above, if you were to start with 0.250 M N_2O_5 , how much is left after 10.0 hours?

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln[A] = -(3.7 \times 10^{-5} \text{ s}^{-1})(3.6 \times 10^4 \text{ s}) + \ln[0.250]$$

$$[A] = 0.0660 \text{ M}$$

1st order reaction



- Write the overall rate expression for this first order reaction.

$$\text{rate} = k[\text{N}_2\text{O}]^1$$

*Note that the exponent does not match the coefficient in front of N_2O . By just looking at the overall balanced equation, you cannot tell the order of the reaction.

- The half-life of N_2O at 1000 K is 0.912 seconds. Determine the rate constant for the above reaction.

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

$$0.912 = \frac{0.693}{k}$$

$$k = 0.76 \text{ s}^{-1}$$

- Using the information above, if you were to start with 1.50 M N_2O_5 , how much is left after 20 seconds?

$$\ln[A] = -kt + \ln[A]_0$$

$$\ln[A] = -(0.76 \text{ s}^{-1})(20 \text{ s}) + \ln[1.50]$$

$$[A] = 3.76 \times 10^{-7} \text{ M}$$

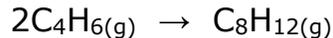
- Using the equation $\ln[A] = -2k't + \ln[A]_0$ and the information above, calculate k' .

$$k = 2k'$$

$$0.76 \text{ s}^{-1} = 2k'$$

$$0.38 \text{ s}^{-1} = k'$$

2nd order reaction



- Write the overall rate expression given that the experimentally determined reaction of the dimerization of butadiene is second order.

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

*Note that in this example the exponent does match the coefficient in front of C_4H_6 . However, this is just a coincidence. By just looking at the overall balanced equation, you cannot tell the order of the reaction.

- The dimerization reaction of butadiene is second order and has a rate constant of $0.0140\text{M}^{-1}\cdot\text{s}^{-1}$ at 500°C . Determine the C_4H_6 concentration after 115.0 seconds if the initial concentration of C_4H_6 is 0.0500 M.

$$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$$

$$\frac{1}{[\text{A}]} = (0.0140\text{M}^{-1}\cdot\text{s}^{-1})(115.0\text{ s}) + \frac{1}{[0.0500]}$$

$$\frac{1}{[\text{A}]} = 21.6$$

$$[\text{A}] = \mathbf{0.0463\text{ M}}$$

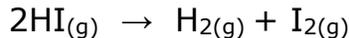
- Using the information above, calculate the half-life for the dimerization reaction of butadiene when the initial concentration of C_4H_6 is 0.0500M.

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

$$t_{1/2} = \frac{1}{(0.0140\text{M}^{-1}\cdot\text{s}^{-1})[0.0500]}$$

$$t_{1/2} = \mathbf{1430\text{ s}}$$

2nd order reaction



- Write the overall rate expression for this experimentally determined second order reaction.

$$\text{rate} = k[\text{HI}]^2$$

- This second order reaction has a rate constant of $6.4 \times 10^{-9} \text{ M}^{-1} \cdot \text{s}^{-1}$ at 500 K. Determine the concentration of HI after 90 days if the initial concentration of C_4H_6 is 0.850 M.

$$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$$

$$\frac{1}{[\text{A}]} = (6.4 \times 10^{-9} \text{ M}^{-1} \cdot \text{s}^{-1})(7776000 \text{ s}) + \frac{1}{[0.850]}$$

$$\frac{1}{[\text{A}]} = 1.23$$

$$[\text{A}] = \mathbf{0.816 \text{ M}}$$

- Using the information above, calculate the half-life for the decomposition of HI when the initial concentration of HI is 2.00 M

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

$$t_{1/2} = \frac{1}{(6.4 \times 10^{-9} \text{ M}^{-1} \cdot \text{s}^{-1})[2.00]}$$

$$t_{1/2} = \mathbf{7.8 \times 10^7 \text{ s}}$$

- Using the equation $\frac{1}{[\text{A}]} = 2k't + \frac{1}{[\text{A}]_0}$ and the information above, calculate k' and discuss whether this reaction is kinetically favorable.

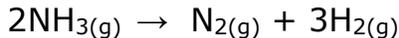
$$k = 2k'$$

$$6.4 \times 10^{-9} \text{ M}^{-1} \cdot \text{s}^{-1} = 2k'$$

$$\mathbf{3.2 \times 10^{-9} \text{ M}^{-1} \cdot \text{s}^{-1} = k'}$$

This reaction is kinetically unfavorable and will take a long time to occur as the rate constant is $\sim 10^{-9}$: the smaller the rate constant, the slower the reaction.

Zero-order reaction



- The above reaction, known as the reverse Haber Bosh process takes place on a hot platinum surface. Write the overall rate expression for this zero order reaction.

$$\text{rate} = k[\text{NH}_3]^0$$

*Note that the exponent does not match the coefficient in front of NH_3 . By just looking at the overall balanced equation, you cannot tell that this is a zero order reaction.

- At a given temperature, the rate constant for the decomposition of ammonia is $5.63 \times 10^{-4} \text{ M}\cdot\text{s}^{-1}$. Determine the initial concentration of NH_3 , if after 90.0 seconds the remaining concentration was 0.599 M.

$$[A] = -kt + [A]_0$$

$$[0.599] = -(5.63 \times 10^{-4} \text{ M}\cdot\text{s}^{-1})(90.0\text{s}) + [A]_0$$

$$[A]_0 = \mathbf{0.650 \text{ M}}$$

- Using the information above, calculate the half-life for the decomposition of ammonia in the reverse Haber Bosh process if the initial concentration of ammonia was 0.350 M.

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

$$t_{1/2} = \frac{0.350 \text{ M}}{2(5.63 \times 10^{-4} \text{ M}\cdot\text{s}^{-1})}$$

$$t_{1/2} = \mathbf{311 \text{ s}}$$

Radioactive Decay

- In microbiology and physics labs, we frequently solve problems about carbon dating and radioactive decay. Radioactive decay is a first order reaction. In these types of problems, the rate constant k is referred to as the decay constant, and N is the number of radioactive nuclei.

Differential Rate Law

$$\text{Rate} = \frac{-dN}{dt} = kN$$

Separate the variables

$$\frac{dN}{N} = -k dt$$

Integrate both sides of the equation

$$\int \frac{dN}{N} = \int -k dt = -k \int dt$$

Indefinite integral constant, b

$$\ln N = -kt + b$$

At time $t = 0$, $b = \ln N_0$ where N_0 is the initial number of radioactive nuclei.

Integrated Rate Law (linear form)

$$\ln N = -kt + \ln N_0$$

To more clearly see the exponential relationship between time, t , and the number of radioactive nuclei, N , we can convert the integrated first-order rate-law (linear form) to its non-linear exponential form:

Raise both sides to the power of e

$$e^{\ln N} = e^{-kt} e^{\ln N_0}$$

Simplify, and obtain non-linear form

$$N = N_0 e^{-kt}$$

One can also then write the non-linear differential rate law:

$$\text{Rate} = \frac{-dN}{dt} = kN = k[N]_0 e^{-kt}$$

- Carbon-14 dating is used to determine the age of various objects and has a half-life of 5730 years. If a sample today contains 0.096 mg of ^{14}C , how much ^{14}C was present in this sample 12,530 years ago?

Hint: To simplify, let mass of ^{14}C = number of radioactive nuclei, N

$$t_{1/2} = \frac{0.693}{k} = 5730 \text{ years}$$

$$k = 1.21 \times 10^{-4} \text{ year}^{-1}$$

$$\ln N = -kt + \ln N_0$$

$$\ln(0.096 \text{ mg}) = -(1.21 \times 10^{-4} \text{ year}^{-1})(12530 \text{ year}) + \ln N_0$$

$$N_0 = 0.437 \text{ mg}$$

Population Growth: Bacteria

- In biology labs, we study bacteria growth under various conditions. Population growth is mathematically equivalent to a first order reaction, but the slope is positive because we are modelling population growth. In these types of problems, the rate constant k is referred to as the growth constant, and N is the number of bacteria and some time, t .

Integrated Rate Law

$$\ln N = kt + \ln N_0$$

Raise both sides to the power of e

$$e^{\ln N} = e^{kt} e^{\ln N_0}$$

Simplify to get exponential form

$$N = N_0 e^{kt}$$

- Suppose the initial number of bacteria in your culture dish is 1.40 million. You check back in an hour and the number of bacteria has increased to 10.35 million. What is the growth rate of this bacterial species (per min)?

One can use the linear or exponential equation above where the initial number of bacteria is N_0 and the number of bacteria after an hour is N .

$$N = N_0 e^{kt}$$

$$[10.35] = [1.40]e^{k(60 \text{ min})}$$

$$7.39 = e^{(60 \text{ min})k}$$

$$\ln(7.39) = \ln e^{60k}$$

$$2.00 = 60k$$

$$k = 0.033 \text{ min}^{-1}$$

$$= 3.3\% \text{ min}^{-1}$$

Drug Concentration

- In biology labs, we study the effectiveness of the body to metabolize certain administered drugs. The body's metabolism of drugs can be defined as a first order reaction. In these types of problems, the rate constant k is characterized as the removal rate of the drug through metabolism or excretion, and C is the concentration of the substance in the body.

Integrated Rate Law

Raise both sides to the power of e

Simplify to get exponential form

$$\ln[C] = -kt + \ln[C]_0$$

$$e^{\ln[C]} = e^{-kt} e^{\ln[C]_0}$$

$$[C] = [C]_0 e^{-kt}$$

- Patients diagnosed with depression have a decreased concentration of serotonin in their brain. To help increase this concentration, doctors administer Selective Serotonin Reuptake Inhibitors (SSRIs) to the patients. Normal levels of serotonin in a healthy individual range from 101-283 ng/ml. Serotonin is metabolized by the body at a rate of $9.63 \times 10^{-6} \text{ s}^{-1}$. Assume that when the SSRI is administered, the serotonin concentration increases to 175.0 ng/ml. How long will it take for the serotonin concentration to fall below 100.0 ng/ml?

$$[C] = [C]_0 e^{-kt}$$

$$[100.0] = [175.0] e^{-(9.63 \times 10^{-6} \text{ s}^{-1})t}$$

$$0.571 = e^{-(9.63 \times 10^{-6} \text{ s}^{-1})t}$$

$$\ln 0.571 = \ln e^{-(9.63 \times 10^{-6} \text{ s}^{-1})t}$$

$$-0.560 = -9.63 \times 10^{-6} t$$

$$t = 5.81 \times 10^4 \text{ s}$$