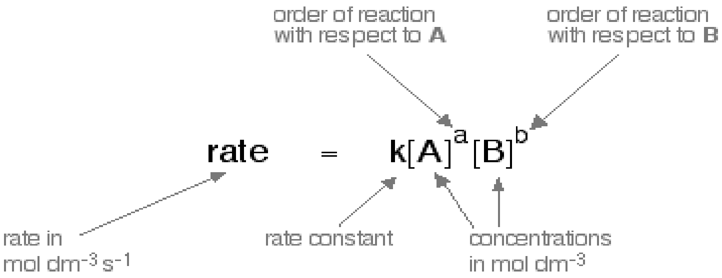
Lecture 34

Rate Laws

A rate law is an expression that relates the reaction rate to the concentrations of the chemical species present in the reaction mixture, may include reactants, products and catalysts (but not reactive intermediates). Many reactions follow a simple rate law in which the rate is proportional to the product of the concentrations raised to some power. The overall order is the sum of the individual orders.



K is a constant that has a specific value for each reaction. The value of k is determined experimentally. K is unique for each reaction. The value of k changes with the change in temperature. Exponents tell the order of the reaction with respect to each reactant. The overall reaction order can be found by adding the exponents on the reactants in the rate law. For example

$$rate = k\left[NH_4^+\right]^1\left[NO_2^-\right]^1$$

Over all the reaction is second order reaction.

Integrated Rate Laws:

The differential rate law describes how the rate of reaction varies with the concentrations of various species, usually reactants, in the system. The rate of reaction is proportional to the rates of change in concentrations of the reactants and products; that is, the rate is proportional to a derivative of a concentration.

To illustrate this point, consider the reaction

$$A \rightarrow B$$

The rate of reaction, *r*, is given by

$$R = -d\,[A]/\ d\,t$$

Suppose this reaction obeys a first-order rate law:

$$r = k\,[\mathrm{A}]$$

This rate law can also be written as

$$R= \frac{-d\,[A]}{d\,t} = k\,[A]$$

This equation is a differential equation that relates the rate of change in a concentration to the concentration itself. Integration of this equation produces the corresponding **integrated rate law**, which relates the concentration to time. When you viewed concentration-time curves in previous pages, you viewed the integrated rate laws.

$$[dA]/[A]= -kd$$

At $t = 0$, the concentration of A is $[A]_0$. The integrated rate law is thus

$[A] = [A]_0\, e^{-k\,t}$

Experimentally one almost always measures how the concentration of a reactant or product changes as the reaction progresses. The experimental data suffers from random error and frequently one only collects points infrequently. Consequently it is difficult or impossible to determine the slope accurately.

The first-order integrated rate law:

The integrated rate law for a first-order reaction

A → products

is a common example of the law of exponential change. For a reactant A, its concentration $[A]_t$ at time t is given by

$[A]_t = [A]_o \times e^{-kt}$ in which $[A]_o$ is its initial concentration and k is the first-order rate constant.

The "e" in the exponential term is of course the base of the natural logarithms, and the negative sign in its exponent means that the value of this term diminishes as t increases, as we would expect for any kind of a decay process. A more convenient form of the integrated rate law is obtained by taking the natural logarithm of both sides:

$\ln\,[A] = -kt + \ln\,[A]_o$(4-1)

This has the form of an equation for a straight line

$y = mx + b$

In which the slope *m* corresponds to the rate constant *k*. This means that, for a first-order reaction, a plot of ln [A] as a function of time gives a straight line with a slope of –*k*.

Second-order reactions:

It states that the sum of the exponents in the rate law is equal to two. Formation of double-stranded DNA is a second order kinetics. It is also in the form of

$$y = mx + b$$

Similarly, integrating the rate law for a process that is second-order in reactant A:

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

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

So if a process is second-order in A, a plot of 1/[A] vs. t will yield a straight line with a slope of k then the reaction is First order: If a reaction is first-order, a plot of ln [A]t vs. t will yield a straight line with a slope of -k.

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

Determining Reaction Order:

Nitrogen dioxide gas, $NO_{2(g)}$, decomposes to form nitric oxide gas, $NO_{(g)}$, and oxygen gas, $O_{2(g)}$.

$$2NO_{2(g)} \rightarrow 2NO_{(g)} + O_{2(g)}$$

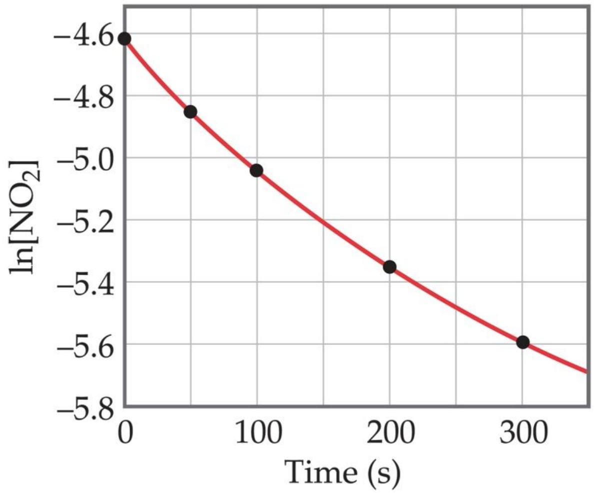
The decomposition at 300°C yields the following data:

Time (s)	$[NO_2]$, M
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Graphing ln [NO2] vs. t yields:

The plot is not a straight line, so the process is not first-order in [A] and does not fit according to equation

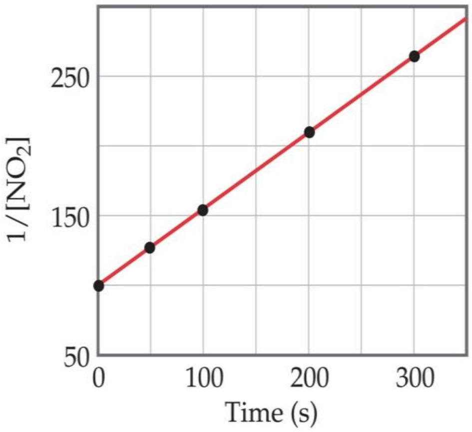
$$ln[A]_t = -kt + ln[A]_0$$



A graph of 1/[NO2] vs. t gives this plot:

This is a straight line curve therefore; the process is second-order in [NO2] and follow the equation

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



Half Life:

The half-life of a reaction, t1/2, is the amount of time needed for a reactant concentration to decrease by half compared to its initial concentration. Its application is used in chemistry and medicine to predict the concentration of a substance over time. Because [A] at $t_{1/2}$ is one-half of the original [A], $[A]_t = 0.5\,[A]_0$. The half-life does not depend on $[A]_0$. For a first-order process, set [A]t=0.5 [A]0 in integrated rate equation.

$$ln\frac{0.5\,[A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$ln(0.5) = -kt_{\frac{1}{2}}$$

$$ln(2) = 0.693 = -kt_{\frac{1}{2}} \qquad \boxed{\frac{0.693}{k} = t_{\frac{1}{2}}}$$

For a second-order process, set [A]t=0.5 [A]0 in 2nd order equation.

$$\frac{1}{0.5\,[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

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

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{\frac{1}{2}} \qquad \boxed{\frac{1}{k\,[A]_0} = t_{\frac{1}{2}}}$$

References:

http://www.chem1.com/acad/webtext/dynamics/dynamics-2.html
http://www.ausetute.com.au/ratelaw.html
http://www.chem1.com/acad/webtext/dynamics/dynamics-2.html
http://www.chm.davidson.edu/vce/kinetics/integratedratelaws.html