Chapter 3: Kinetics

The hydrolysis of ethylacetate by sodium hydroxide,

$$CH_3COOCH_2CH_3 + OH^- \rightarrow CH_3COO^- + CH_2CH_3OH$$

is proposed to follow an addition-elimination mechanism. The time course for the reaction with initial concentration of hydroxide at 0.0100 M and initial ethylacetate at 0.02656 M is given below, as determined by conductivity measurements. Determine the rate law for the process. In the next chapter we will discuss how to verify that the rate law is consistent with the proposed mechanism.

t (min)	0	1	2	3	4	5	6
$[OH^-]/10^{-3}$ M	10.000	7.307	5.467	4.285	3.348	2.634	2.133
t (min)	7	8	9	10	11	12	
$[OH^-]/10^{-3}$ M	1.698	1.361	1.131	0.918	0.754	0.630	

The rates of chemical reactions play a critical role in the maintenance of natural bio-geochemical cycles and the fate of environmental pollutants. The rates of processes in living cells are carefully controlled by the regulation of enzymatic catalysis. The tailoring of the properties of polymeric systems involves the careful control of the kinetics of polymerization. The competition between kinetic and equilibrium control of organic synthetic reactions often determines the production of useful products. The route to increased energy efficiency in industrial production is often through the development of new transition metal catalysts that lower the activation energy demand and increase the specificity of chemical reactions. A careful description of the rates of chemical processes is critical for many applications. How do we characterize and control the rates of chemical reactions?

You have already had an introduction to chemical kinetics in your General Chemistry course. Please review your General Chemistry text chapter on chemical kinetics, so that we don't need to repeat that introductory information. We now want to expand beyond that elementary treatment.

A chemical kinetics study has three stages:

1. The determination of the empirical rate law.
2. The determination of the mechanism of the reaction.
3. The determination of the rate constants for each mechanistic step through first-principles theoretical calculations.

Stage 1: Consider the example reaction:

$$H_2\,(g) + I_2\,(g) \rightarrow 2\,HI\,(g)$$

The **rate law** expresses the concentration or partial pressure dependence of the rate of the reaction. The experimentally determined rate law in terms of partial pressures is:

$$\text{rate} = \upsilon = -\frac{dP_{H_2}}{dt} = k\,P_{H_2}\,P_{I_2}$$

or in terms of gas phase concentrations:

$$\upsilon = -\frac{d[H_2]}{dt} = k\,[H_2]\,[I_2] \qquad \text{or equivalently} \qquad \upsilon = -\frac{d\,c_{H_2}}{dt} = k\,c_{H_2}\,c_{I_2}$$

where k is the rate constant. The symbol υ will be used to symbolize the rate of the reaction. The **order** of the reaction with respect to each constituent is the exponent of the concentration term in the rate law. The **overall order** is the sum of the orders with respect to each reactant. In other words, this reaction is first order in H_2, first order in I_2, and second order overall. Remember that the reaction orders cannot be predicted from the reaction stoichiometry, because the reaction may occur in more than one mechanistic step. The reaction orders can only be determined by experiment. This specific rate constant might also be written as k_2, indicating that the reaction is second order overall. However, the subscripts for rate constants are really just for convenience and have no theoretical significance. For example, for another system k_2 might specify that it is the second rate constant in a series of reactions.

The order of the reaction with respect to a substance is often 1, 2, or rarely 3. However, reaction orders can also be simple fractions like ½ or ¾ or any rational number and also negative. A negative order shows that the reaction rate decreases with increasing concentration or partial pressure of the species. Reactants, products, the solvent, and catalysts can appear in rate laws. An example with a product appearing in the rate law and also a negative non-integer order is:

$$2\,SO_2\,(g) + O_2\,(g) \rightarrow 2\,SO_3\,(g) \qquad \upsilon = \frac{1}{2}\frac{d[SO_3]}{dt} = k\,[SO_2]\,[SO_3]^{-1/2}$$

An example with a catalyst is the decomposition of hydrogen peroxide, catalyzed by iodide ion:

$$2\,H_2O_2\,(aq) \xrightarrow{I^-} 2\,H_2O\,(l) + O_2\,(g) \qquad \upsilon = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k\,[H_2O_2]\,[I^-]$$

The I^- ion does not appear in the reaction stoichiometry, but does appear in the rate law.

Stage 2: After the empirical rate law is determined, a **mechanism** is developed that agrees with the experimental rate law. For example, one possible mechanism for the $H_2 + I_2$ reaction is:

$$I_2\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,I\,(g)$$

$$H_2\,(g) + I\,(g) \xrightarrow{k_2} HI\,(g) + H\,(g)$$

$$H\,(g) + I_2\,(g) \xrightarrow{k_2'} HI\,(g) + I\,(g)$$

The mechanism is the sequence of **elementary** steps that describe the collisions that take place during the course of the reaction. The number of molecules involved in each collision is called the **molecularity**. The first step in the forward direction, $I_2 \rightarrow 2\,I$, is **unimolecular**. The first step in the reverse direction, $2\,I \rightarrow I_2$, is **bimolecular**. The second and third steps are both bimolecular. The steps in a complete mechanism should add to give the overall reaction. There may be more than one mechanism that agrees with the experimental rate law. For example, an alternate mechanism for $H_2 + I_2$ is:

$$I_2\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2I\,(g) \qquad H_2\,(g) + 2\,I\,(g) \xrightarrow{k_3} 2HI\,(g)$$

A definitive conclusion about the actual mechanism for the reaction may be difficult. Or, several mechanisms may be operative depending on the reaction conditions. Reaction mechanisms are the subject of the next chapter.

Stage 3: Once a mechanism has been postulated, calculations of the reaction dynamics are used to predict the rate constants for the elementary steps in the mechanism. These calculations are often based on molecular orbital calculations and statistical mechanical theories for the reaction dynamics. We will return to reaction dynamics at the end of this text after we have covered quantum mechanics and statistical mechanics.

We first consider how to determine the reaction rate law.

3.1 The Rate Law Expresses the Concentration Dependence of the Rate of the Reaction

The rate law may be expressed in terms of the rate of appearance of a product or the rate of disappearance of a reactant. The rates expressed in terms of different species are related by the stoichiometric coefficients for the balanced chemical reaction.

The Expression of Chemical reactions: Consider the general reaction:

$$a\,A + b\,B \rightarrow c\,C + d\,D \qquad 3.1.1$$

Let the number of moles of A change by dn_A; or in general for species i the change is dn_i. The changes are related through the stoichiometric coefficients:

$$\frac{-1}{a}\,dn_A = \frac{-1}{b}\,dn_B = \frac{1}{c}\,dn_C = \frac{1}{d}\,dn_D \equiv d\xi \qquad 3.1.2$$

These relationships define the **change in the extent of the reaction**, $d\xi$. We use the extent of the reaction to measure the reaction progress, because the extent is independent of the stoichiometry. The **extent** of the reaction, ξ, varies from 0 to 1 mol during the course of the reaction as written, corresponding to a moles of A reacting to produce c moles of C. Eq. 3.1.2 can be applied to any single step reaction, multi-step reactions that don't involve stable intermediates, and reactions close to equilibrium, since the concentrations of intermediates are negligible near equilibrium. The stoichiometric coefficients are unitless, giving the units for ξ as moles. The **stoichiometric coefficients** are symbolized as ν_i for each constituent i. The ν_i are defined as negative for a reactant and positive for a product. With the associations $\nu_A = -a$, $\nu_B = -b$, $\nu_C = c$, and $\nu_D = d$, in general:

$$\frac{1}{\nu_i}\,dn_i = d\xi \qquad 3.1.3$$

or equivalently solving for the change in moles:

$$dn_i = \nu_i\,d\xi \qquad 3.1.4$$

The rate law is usually expressed in terms of concentrations or partial pressures, which are intensive variables, so that the rate law holds for any size system. Dividing Eq. 3.1.3 by the volume:

$$\frac{1}{\nu_i}\,d(n_i/V) = \frac{1}{\nu_i}\,dc_i = \frac{1}{V}\,d\xi \qquad 3.1.5$$

and taking the derivative with respect to time gives the **rate** of the reaction in terms of changes in concentration:

$$\upsilon = \frac{1}{\nu_i}\frac{dc_i}{dt} = \frac{1}{V}\frac{d\xi}{dt} \qquad 3.1.6$$

Partial pressures and molal concentrations can also be used. The rate defined by this last equation is sometimes called the **instantaneous rate**, which is just the derivative of the concentration versus time curve at the time of interest. The **average rate** for a reaction during the time interval from t_1 to t_2 is given by the concentrations at time t_1 and t_2, $c_i(t_1)$ and $c_i(t_2)$, respectively:

$$\bar{\upsilon} = \frac{1}{\nu_i}\frac{c_i(t_2) - c_i(t_1)}{t_2 - t_1} \qquad \text{at } \bar{t} = \frac{t_1 + t_2}{2} \quad \text{and} \quad \bar{c} = \frac{c_i(t_1) + c_i(t_2)}{2} \qquad 3.1.7$$

The average rate corresponds to a time and concentration half-way through the interval, Figure 3.1.1.

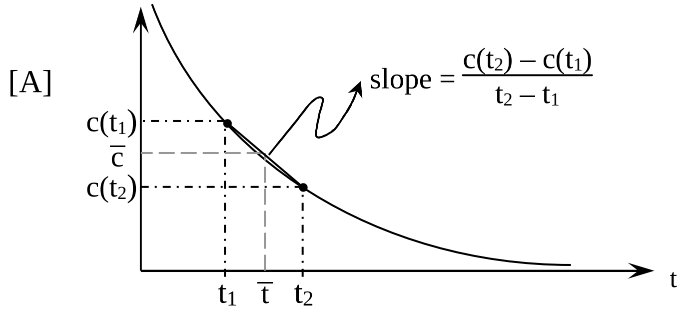


Figure 3.1.1: The average rate corresponds to the midpoint of the time interval.

The Time Course for the Reaction is Determined Experimentally: The starting point for the determination of the rate law is the measurement of the concentration of a reactant or product as a function of time. The concentrations can be measured by many different analytical techniques. We will focus on UV/visible absorption spectroscopy, fluorescence, and conductivity. To determine the rate law, there are several options.

1. The **Integral Method**: The experimental time course can be compared to the integrated form of different possible rate laws.
2. The **Half-time Method**: The variation of the half-times of the reaction with initial concentration can be compared to predictions from the possible rate laws.
3. The **Differential Method**: The differential method directly follows the average rate of the reaction as a function of the concentrations. The initial rate method that you learned in your General Chemistry course is a version of the differential technique.

We first consider the integral and half-time methods. For these methods we need to find the **integrated rate laws**, which express the concentrations of the reactants and products as a function of time.

3.2 Determining the Rate Law: Integrated Rate Laws and Half-Times

1st Order Reactions: Consider a first order reaction of the form:

$$A \xrightarrow{k_1} B \tag{3.2.1}$$

with first-order rate constant k_1. Assume a first-order rate law written in terms of the rate of disappearance of the reactant:

$$-\frac{d[A]}{dt} = k_1 [A] \tag{3.2.2}$$

Multiplying both sides of this equation by dt gives:

$$d[A] = -\, k_1[A]\, dt \tag{3.2.3}$$

which with reference to general pattern ℘***1*** we recognize as a *simple exponential process*. The limits for the integration are at t = 0 the initial concentration of A is $[A]_o$ and at time t the concentration of A is given as [A]:

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -\int_0^t k_1\, dt \tag{3.2.4}$$

Then using ℘***1*** we can immediately write the **integrated rate law** as:

$$\ln\left(\frac{[A]}{[A]_o}\right) = -\, k_1 t \tag{3.2.5}$$

Solving for [A] gives:

$$[A] = [A]_o\, e^{-k_1 t} \tag{3.2.6}$$

which we recognize as a simple exponentially decreasing function of time, Figure 3.2.1a. Fitting time course data to Eq. 3.2.6 is used to verify first-order behavior. Eq. 3.2.5 shows that we can also verify first-order behavior by plotting the experimental data as ln [A] versus t. Solving Eq. 3.2.5 for ln [A] and comparing to the general form of a straight line gives:

$$\begin{aligned} \ln [A] &= -\, k_1 t + \ln [A]_o \\ y &= m\, x + b \end{aligned} \tag{3.2.7}$$

Associating the independent variable x with t, the slope is $m = -\, k_1$ and the intercept $b = \ln [A]_o$. If the resulting plot is a straight line, as in Figure 3.2.1b, the reaction is first order in A.

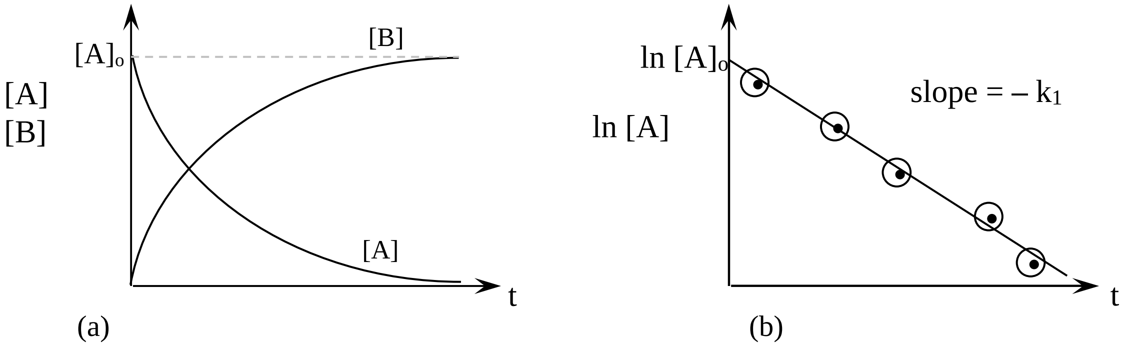


Figure 3.2.1: First-order kinetics. (a) Integrated rate law, (b) A linear plot of ln [A] vs. t verifies first-order behavior.

We could also follow the appearance of the product. From the one-to-one stoichiometry of this reaction, the current concentrations of the reactant and product are related by:

$$[A]_o = [A] + [B] \tag{3.2.8}$$

where [A] and [B] are the concentrations of the reactant and product at time t. We can then calculate the concentration of B by difference, $[B] = [A]_o - [A]$:

$$[B] = [A]_o - [A] = [A]_o\,(1 - e^{-k_1 t}) \tag{3.2.9}$$

where we have substituted Eq. 3.2.6 for [A]. The concentration of B is also shown in Figure 3.2.1a. For the asymptotic concentration of [B], for long times, $t \rightarrow \infty$, $e^{-k_1 t} \rightarrow 0$, and $[B] \rightarrow [A]_o$.

1st Order Reaction Half-Times: Another way to characterize first-order behavior is to find the half-time of the reaction. The half-time, $t_{½}$, of the reaction is the time necessary for the initial concentration of the reactant to decrease to one-half of its initial value. Substituting $[A] = [A]_o/2$ into Eq. 3.2.4 gives at the half-time:

$$\ln\left(\frac{[A]_o/2}{[A]_o}\right) = -\,k_1\,t_{½} \tag{3.2.10}$$

Solving for the half-time gives:

$$t_{½} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1} \tag{3.2.11}$$

Notice that for a first-order reaction the half-time is independent of the initial concentration. In other words, the time necessary for the concentration to decrease from 1.0 M to 0.5 M is the same as the time from 1.0×10^{-6} M to 0.5×10^{-6} M. Another characteristic of simple exponential decay is that the concentration decreases by a factor of two for every successive half-time, Figure 3.2.2.

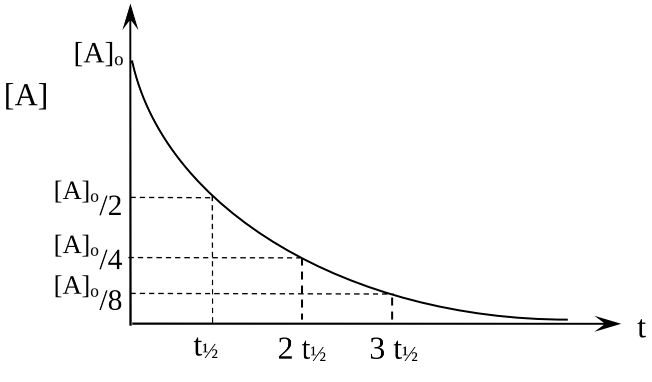


Figure 3.2.2: For a first-order reaction, the concentration decreases by a factor of two for every successive half-time.

Radioactive decay is a first-order kinetic process. The number of disintegrations per second of the radionuclide decreases exponentially with time. The half-time for the kinetic process is called the half-life of the particular radionuclide. The half-life of a radionuclide is a distinguishing characteristic. The half-life of uranium-238 is 4.5 billion years and of polonium-212 is 0.305 μs.

Many other processes follow first-order kinetics. Fluorescence emission follows first-order kinetics. The **fluorescence lifetime** is defined as $\tau_f = 1/k_f^*$, where k_f^* is the effective rate constant for fluorescence decay. The intensity of fluorescence emission, I, is given as:

$$I = I_o\, e^{-k_f t} = I_o\, e^{-t/\tau_f} \qquad 3.2.12$$

where I_o is the initial fluorescence intensity after a short pulse of exciting light. Pulsed lasers, pulsed light emitting diodes, and xenon flash lamps are commonly used as time-resolved fluorescence excitation sources. Many biological assays are based on changes of fluorescence lifetimes. Please see the next chapter for a more complete analysis of fluorescence lifetimes.

One useful interpretation of the fluorescence lifetime and exponential decay in general is to notice that when the time is equal to τ_f the exponential factor decreases by e^{-1}. The numerical factor is $e^{-1} = 1/e = 0.368$. The lifetime, τ_f, is often called the “1/e time.” All first-order processes have a corresponding lifetime. For chemical kinetics, the 1/e time is equal to 1/k. The time necessary for the concentration of the reactant in a first-order chemical reaction to drop to 0.368 of its initial concentration is $\tau = 1/k$. Notice that the lifetime and the half-time of a first-order process are distinct, but directly related, characteristics; $t_{½} = 0.6931\ \tau$.

Boundary Conditions: We used general pattern ***℘1*** to quickly derive the integrated rate law for a first-order reaction. This derivation used a definite integral with the limits of integration: at t = 0 the initial concentration of A is $[A]_o$ and at time t the concentration of A is given as [A]. The traditional method of solving differential equations does the integration in a different order. First the equation is integrated using an indefinite integral and then the constant of integration is fixed using **boundary conditions**. Let’s repeat the derivation of Eq. 3.2.7 to highlight the difference in procedure. First, as in ***℘1***, we do the separation of variables by dividing both sides of Eq. 3.2.3 by [A]:

$$\frac{1}{[A]}\, d[A] = -\, k_1\, dt \qquad 3.2.13$$

Then we do the indefinite integrals:

$$\int \frac{1}{[A]}\, d[A] = -\int k_1\, dt \qquad 3.2.14$$

to find:

$$\ln [A] + c' = -k_1 t + c'' \qquad 3.2.15$$

where c' and c'' are the integration constants for the two integrals. We can combine the two integration constants as c = c'' – c' to give:

$$\ln [A] = -k_1 t + c \qquad 3.2.16$$

To find the integration constant we now apply the boundary condition: at t=0 the concentration of A is the initial concentration, $[A] = [A]_o$. Setting t = 0 and $[A] = [A]_o$ in Eq. 3.2.16 at the initial boundary gives:

$$c = \ln [A]_o \qquad 3.2.17$$

Substituting this value for c back into Eq. 3.2.15 gives the final result:

$$\ln [A] = -k_1 t + \ln [A]_o \tag{3.2.18}$$

This last equation is the same as Eq. 3.2.7. The choice of the method to use, definite integral or indefinite integral with a boundary condition, is a historical choice. Historically, chemical kinetics was developed using indefinite integrals with boundary conditions, which is also the normal presentation of the general theory of differential equations. Thermodynamics was developed using definite integrals. You may use either method when you do the homework problems. Let's continue on to determine the integrated rate laws for second-order reactions and then get back to the experimental data.

2nd Order Reactions: There are two general types of second-order reactions: $A \rightarrow B + C$ and $A + B \rightarrow C + D$. We tackle the type with a single reactant first. Assume the following reaction is second-order in A:

$$A \rightarrow \text{products} \tag{3.2.19}$$

The rate law is:

$$-\frac{d[A]}{dt} = k_2 [A]^2 \tag{3.2.20}$$

We can separate the variables by multiplying both sides of the equation by dt and dividing both sides of the equation by $[A]^2$;

$$\frac{-1}{[A]^2}\, d[A] = k_2\, dt \tag{3.2.21}$$

Note that the integral on the left is (see addendum 1.5, Table 1.5.1):

$$\int \frac{-1}{[A]^2}\, d[A] = \frac{1}{[A]} + c' \tag{3.2.22}$$

Taking the indefinite integral of both sides and combining the integration constants gives:

$$\frac{1}{[A]} = k_2 t + c \tag{3.2.23}$$

To calculate the integration constant, we apply the boundary condition at $t = 0$ then $[A] = [A]_o$. Setting $t = 0$ and $[A] = [A]_o$ in Eq. 3.2.23 gives:

$$c = \frac{1}{[A]_o} \tag{3.2.24}$$

Substituting this integration constant back into Eq. 3.2.23 gives the integrated rate law:

$$\frac{1}{[A]} = k_2 t + \frac{1}{[A]_o} \tag{3.2.25}$$

This equation is in the form of a straight line, Figure 3.2.3, with t as the independent variable. We can verify second-order behavior if a plot of the experimental data as $1/[A]$ versus t gives a straight line, with slope $m = k_2$ and intercept $b = 1/[A]_o$. The time course of the reaction can be determined by solving Eq. 3.2.25 for [A]:

$$[A] = \frac{1}{\frac{1}{[A]_o} + k_2\, t} = \frac{[A]_o}{1 + k_2\, [A]_o\, t} \qquad 3.2.26$$

The time courses of first- and second-order process are indistinguishable by eye; both plots of [A] versus t look similar. The last equation is used for non-linear fitting of experimental data.

Eq. 3.2.25 is often rearranged by subtracting $1/[A]_o$ from both sides of the equation to give a form that can be compared to Eq. 3.2.5 for a first-order reaction:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = k_2\, t \qquad 3.2.27$$

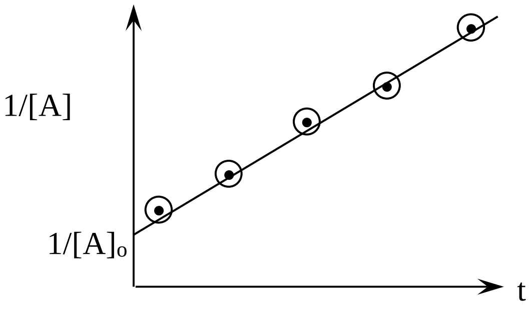


Figure 3.2.3: Second-order kinetics: A linear plot of 1/[A] vs. t verifies second-order behavior.

2nd Order Reaction Half-Times: Once again we set $t = t_{½}$ and $[A] = [A]_o/2$ in Eq. 3.2.27 to find the reaction half-time:

$$\frac{1}{[A]_o/2} - \frac{1}{[A]_o} = k_2\, t_{½} \qquad 3.2.28$$

Canceling terms gives:

$$\frac{1}{[A]_o} = k_2\, t_{½} \qquad 3.2.29$$

and solving for the half-time gives:

$$t_{½} = \frac{1}{[A]_o k_2} \qquad 3.2.30$$

Notice that the half-time for a second-order process does depend on the initial concentration. The time necessary for the concentration to decrease from 1.0 M to 0.5 M is a million times shorter than the time from $1.0\text{x}10^{-6}$ M to $0.5\text{x}10^{-6}$ M. The dependence of the half-time on initial concentration is an important tool for determining the order of a reaction.

The Effect of Reaction Stoichiometry: The order of the reaction with respect to the various reactants and products cannot be determined from the reaction stoichiometry; however, the reaction stoichiometry still has an effect on the details of the overall rate law. For example, consider two different stoichiometries for a second-order reaction:

$$A \rightarrow B \qquad \text{and} \qquad 2\,A \rightarrow B$$

The rate law for the first 1:1 stoichiometry is:

$$\upsilon = -\frac{d[A]}{dt} = k_2\,[A]^2 \qquad (A \rightarrow B) \qquad 3.2.31$$

and for the 2:1 stoichiometry from Eq. 3.1.2:

$$\upsilon = -\frac{1}{2}\frac{d[A]}{dt} = k_2\,[A]^2 \qquad (2\,A \rightarrow B) \qquad 3.2.32$$

or solving this last equation for the rate of disappearance of A:

$$-\frac{d[A]}{dt} = 2\,k_2\,[A]^2 \qquad (2\,A \rightarrow B) \qquad 3.2.33$$

You might note that sometimes we are lazy, or forgetful, and neglect to write the stoichiometric factor, as in the multiplicative factor of 2 in this last equation. However, for multi-step mechanisms, it is important to use Eq. 3.1.2 to relate the rates for different reactions in a series, so that the reactions are compared on an equal footing and the overall stoichiometry of the reaction is maintained.

Isolation Method and Pseudo-Order Reactions: For complicated reactions it is often useful to simplify the rate law by setting the concentrations of all the reactants except for one in large excess, so the concentrations of everything but the species of interest remain essentially constant. For example, consider reactions of the type A + B → P. With B in large excess, the concentration of B will remain at the initial concentration, $[B] = [B]_o$. The rate law:

$$\upsilon = -\frac{d[A]}{dt} = k\,[A]^n[B]_o^m \qquad 3.2.34$$

can be rearranged to give:

$$\upsilon = -\frac{d[A]}{dt} = (k[B]_o^m)\,[A]^n \qquad 3.2.35$$

and an **effective rate constant** is then defined as $k_{eff} = k[B]_o^m$. The order of the reaction with respect to A can then be determined by comparing the experimental time course to integrated rate laws. As a separate study, the concentration of A can then be held in excess and then the order with respect to B can be determined.

If the solvent is one of the reactants in dilute solution, the concentration of the solvent will remain essentially constant. The concentration of the solvent is often combined with the rate constant. For example, the rate of hydrolysis of sucrose in dilute aqueous solution is first-order in sucrose and first order in H_2O:

$$-\frac{d[\text{sucrose}]}{dt} = k\,[\text{sucrose}][H_2O] = k_{eff}\,[\text{sucrose}] \qquad 3.2.36$$

where $k_{eff} = k[H_2O]$ with the molar concentration of water in dilute solution at ~55.5 M. This reaction is said to be a **pseudo-first order** reaction. The concentration of a catalyst is often essentially constant during the course of a reaction and can be similarly lumped with the rate constant to give a simplified **pseudo-order** rate law.

The isolation method has some drawbacks. The mechanism of the reaction may change with a large excess of one of the reactants. Alternatively, the reaction may have several parallel pathways that shift in importance with concentrations. The isolation method is often used for initial studies. However, the rate law so obtained should be verified by studies with comparable concentrations of all the reactants.

Determining the Reaction Order: Since absorbance is directly proportional to concentration, $A = \varepsilon\ell c$, the absorbance can be used for the curve fitting in place of the concentrations. As a first example, assume that only the reactant absorbs. For a first-order reaction, the $\varepsilon\ell$ term cancels in the numerator and denominator of the ln term in Eq. 3.2.5, so either concentration or absorbance may be used to directly determine the rate constant. For a second-order reaction, substituting $c = A/\varepsilon\ell$ into Eq. 3.2.27 gives:

$$\frac{1}{A} - \frac{1}{A_o} = \frac{k_2}{\varepsilon\ell}\,t \qquad \text{(single absorber)} \qquad 3.2.37$$

where A_o is the initial absorbance. Note that we use [A] for the concentration of A and just A for the absorbance. Then to determine the order of a reaction, absorbance versus time measurements are collected in the laboratory and the data are plotted according to Eqs. 3.2.5, 3.2.7 and 3.2.27. Notice that a plot of 1/A versus t gives a straight line for a second-order reaction with a slope of $k_2/\varepsilon\ell$. Often in the laboratory, the long-time limiting absorbance, A_∞, of a reaction mixture approaches a constant rather than zero. This constant **offset** may be caused by instrumental artifacts like misalignment of the cuvette, calibration drift, or by the constant absorbance of another species in solution. The absorbance of a solution with a constant offset is given by:

$$A = \varepsilon\ell\, c + A_\infty \qquad \text{(constant offset)} \qquad 3.2.38$$

and then the concentration of the species is given by $c = (A - A_\infty)/\varepsilon\ell$. The plots are then made of $\ln(A - A_\infty)$ versus t or alternatively $1/(A - A_\infty)$ versus t.

As a second example, consider a reaction where both the reactant and product absorb. Consider a general reaction of the form A + B → C + D. Assume that both A and C absorb, and let $[C]_o = 0$. During the reaction $[A] = [A]_o - \xi$ and $[C] = \xi$. The absorbance of the mixture at a single wavelength is given by Eq. 2.6.1:

$$A = \varepsilon_A\ell\,([A]_o - \xi) + \varepsilon_C\ell\,\xi \qquad \text{(product and reactant absorb)} \; 3.2.39$$

where ε_A and ε_C are the molar absorption coefficients of A and C, respectively. The following ratio can be used to follow the progress of the reaction:

$$\frac{[A]}{[A]_o} = \frac{[A]_o - \xi}{[A]_o} = \frac{A - A_\infty}{A_o - A_\infty} \qquad \text{(product and reactant absorb)} \; 3.2.40$$

To prove this relationship, substitute Eq. 3.2.39 into the absorbance ratio in this last equation, noting that, because of the 1:1 stoichiometry, $\xi = [A]_o$ at the end of the reaction:

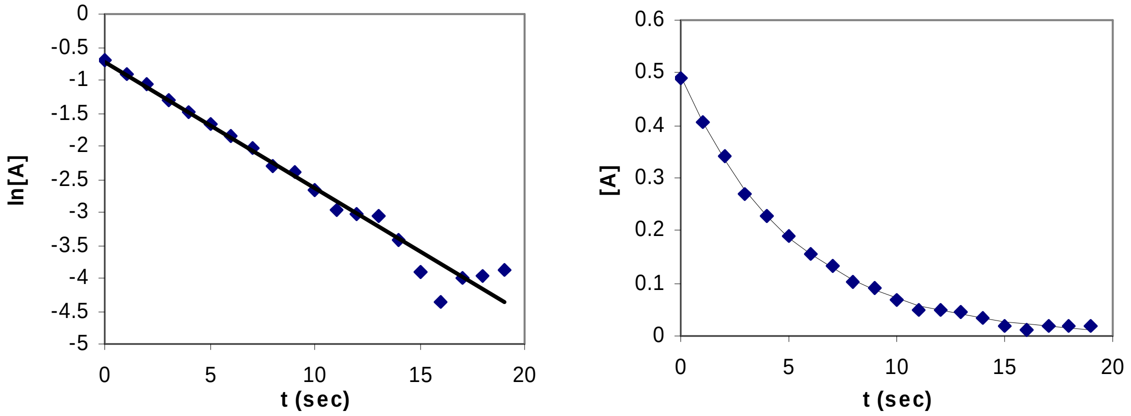
$$\frac{A - A_\infty}{A_o - A_\infty} = \frac{[\varepsilon_a\ell\,([A]_o-\xi) + \varepsilon_c\ell\,\xi] - \varepsilon_c\ell\,[A]_o}{\varepsilon_a\ell\,[A]_o - \varepsilon_c\ell\,[A]_o} = \frac{\varepsilon_a\ell\,([A]_o-\xi) - \varepsilon_c\ell\,([A]_o-\xi)}{(\varepsilon_a\ell - \varepsilon_c\ell)\,[A]_o} = \frac{[A]_o-\xi}{[A]_o} \qquad 3.2.41$$

Alternatively:

$$\frac{[A]_o - [A]}{[A]_o} = \frac{\xi}{[A]_o} = \frac{A_o - A}{A_o - A_\infty} \qquad \text{(product and reactant absorb) } 3.2.42$$

Eqs. 3.2.40 and 3.2.42 can be used interchangeably. Absorbance is not unique. Equations similar to Eq. 3.2.38-42 hold for absorbance, conductivity, fluorescence or any other analytical technique giving data that are directly proportional to concentration and additive for multiple constituents. Eqs. 3.2.40 and 3.2.42 eliminate the need to know the molar absorption coefficients or molar conductivity of the reactants or products for the purposes of verifying the reaction order. Notice however, that the molar absorption coefficient does affect the slope of the plot for a second-order reaction, Eq. 3.2.37.

Finally, while the linear forms of the integrated rate laws are useful for verifying the order of a reaction, non-linear curve fitting is better for calculating the values of rate constants. The linear plot for a first order reaction that has a significant amount of experimental uncertainty, or noise, is shown in Figure 3.2.4a. Notice that the effect of noise increases as the reaction progresses. Linear curve fitting treats all points equally. However, the data points at the beginning of the reaction have less relative uncertainty than data points at the end of the time course, so data points at the beginning of the reaction should be weighted more strongly in the curve fit.



(a) Linear fit (b) Non-linear fit

Figure 3.2.4: A simulated data set with constant absolute error of ±0.010. Non-linear curve fitting gives $k = 0.1934 \pm 0.0023\ \text{sec}^{-1}$ and $[A]_o = 0.4933 \pm 0.0038$ M.

The best way to extract the rate constant is to fit the data directly to Eq. 3.2.6 or Eq. 3.2.26. Another good reason to choose non-linear curve fitting is that the A_∞ value can be treated as a fit parameter, Eq. 3.2.38. Using non-linear curve fitting is often the only way to make an unbiased choice for A_∞, especially if there is significant noise in the long-time portion of the data. Non-linear curve fitting is very easy, Figure 3.2.4b.

www Several on-line applets for non-linear curve fitting are available, including the "Nonlinear Least Squares Curve Fit" applet on the textbook Web site and on the companion CD. Excel spreadsheets are also available to do exponential curve fitting. Many commercial graphics packages are specifically designed for non-linear curve fitting. Appendix 2 gives the formulas.

Non-linear curve fitting procedures give statistically valid estimates for the uncertainties of the fit parameters and an estimate of the correlation coefficient between the fit parameters. For example consider first-order kinetic exponential fitting with fit parameters $[A]_o$ and k. A correlation coefficient between the fit parameters of 0 means that the error in $[A]_o$ has no effect on the error in k. For a correlation coefficient of ±1, the errors in $[A]_o$ and k are completely correlated. For high correlation coefficients, a small change in the value of one of the data points, caused by experimental error, will give a large change in the fit values of both $[A]_o$ and k. Such a complete correlation means that neither parameter estimate is valid. For the example in Figure 3.2.4, the correlation coefficient between the fit parameters $[A]_o$ and k is 0.64. Such a correlation coefficient is quite good for exponential curve fitting. Correlation coefficients larger than 0.95 usually suggest that one of the fit parameters needs to be specified as a fixed parameter, which is independently determined either directly from the data or from another experiment.[1] In some cases algebraic rearrangement of the model equation can decrease fit value correlations.

Half-time Methods: Instead of direct comparison of the time course data to various integrated rate laws, the variation of the half-time of the reaction for changes in initial concentrations of the reactants can be used to establish the order of the reaction. The reaction is run with several different starting concentrations of each reactant and the half-times for the reactions are compared to the values expected for the different reaction orders, Eqs. 3.2.11 and 3.2.30. If the half-time doesn't change as the initial concentration of a reactant is changed, then the reaction is first order. If the half-time is inversely proportional to the initial concentration, the reaction is second order.

Example 3.2.1: *Determine Reaction Order by Comparison to Integrated Rate Laws*
Crystal violet reacts with hydroxide to convert the dye to a colorless form:

$$CV^+ + OH^- \rightarrow CVOH$$

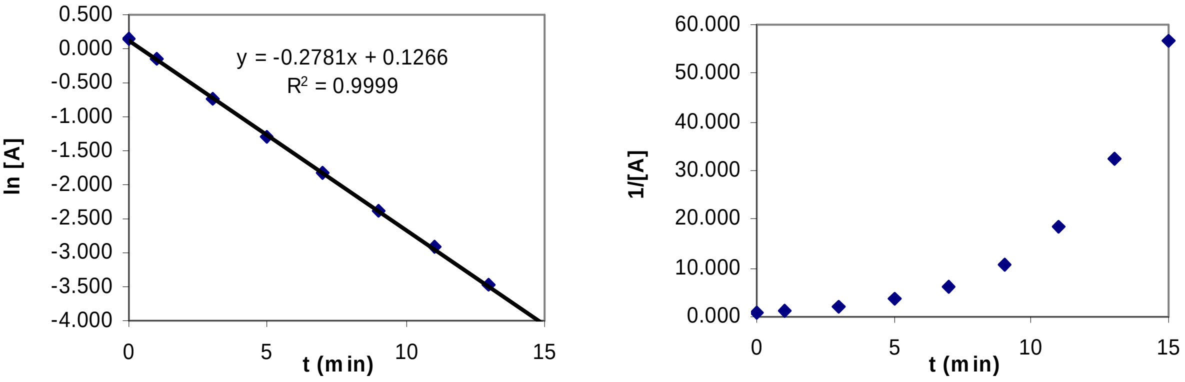
purple colorless

The time course, measured as the absorbance of the solution at 590 nm, is given below for an initial crystal violet concentration of 1.2×10^{-5} M and a hydroxide concentration of 0.0300 M. The long-time absorbance is 0.040. Determine the order of the reaction and the rate constant.

t (min)	0	1	3	5	7	9	11	13	15
A	1.200	0.905	0.526	0.317	0.200	0.133	0.094	0.071	0.058

Answer: This experiment is an example of the isolation method. The concentration of base is large enough that the concentration is essentially constant during the course of the reaction. Using the linear forms of the integrated rate laws, we need to prepare plots according to Eqs. 3.2.7 and 3.2.25. In addition, the absorbance doesn't go to zero; there is an offset in the long-time limit. So Eq. 3.2.38 must be used to cancel the offset. A spreadsheet is set up with columns t, A, and $A - A_\infty$, $\ln(A - A_\infty)$, and $1/(A - A_\infty)$. The corresponding plots are given in Figure 3.2.5.

t (min)	A	A – A∞	ln(A– A∞)	1/(A – A∞)
0	1.200	1.160	0.148	0.862
1	0.905	0.865	-0.146	1.157
3	0.526	0.486	-0.722	2.059
5	0.317	0.277	-1.282	3.604
7	0.200	0.160	-1.833	6.250
9	0.133	0.093	-2.376	10.760
11	0.094	0.054	-2.926	18.649
13	0.071	0.031	-3.484	32.593
15	0.058	0.018	-4.041	56.876



(a) First-order plot

(b) Second-order plot.

Figure 3.2.5: Kinetic plots for crystal violet time course fitting.

The reaction is clearly first order in crystal violet. The effective rate constant is 0.278 ± 0.001 min^{-1}. This reaction is a pseudo-first order reaction. The rate constant is an effective rate constant with $k_{eff} = k[OH^-]_o^m$. If we assume that the reaction is first order in base, m = 1, and solving for k gives:

$$k = \frac{k_{eff}}{[OH^-]_o} = \frac{0.2781\ \text{min}^{-1}}{0.0300\ \text{M}} = 9.27\ \text{M}^{-1}\ \text{min}^{-1}$$

A different k would result if the reaction is second order in base.

Notice that we did not use the R^2 goodness of fit criterion to compare the curves. The overall fit correlation coefficient, either R or R^2, is not designed to be a statistically valid way of comparing the appropriateness of two different models. The overall correlation coefficient is designed to judge the degree of fit to the straight line, not compare two different underlying models.[2] The R^2 statistic is a measure of the null hypothesis that the data is a random scatter of points as compared to a linear function. Using R^2 to choose between two possible kinetic models can lead to incorrect conclusions.[2] Rather, the best way to judge the order of the reaction is to look for systematic deviations from the fit line. In particular, the second-order plot shows significant systematic curvature.

Example 3.2.2: *Non-linear Curve Fitting to Integrated Rate Laws*

Use the data in Example 3.2.1 to do a non-linear curve fit.

Answer: One of the advantages of using non-linear curve fitting is that you can make the A_∞ value a fitted parameter. The "Nonlinear Least Squares Curve Fit" applet on the textbook Web site or on the companion CD is an easy way to do the curve fitting. For first-order fitting, Eq. 3.2.6, with a constant offset is the "a exp(-bx) + c" option in the applet:

a exp(-bx) + c corresponds to $A_o\, e^{-kt} + A_\infty$.

For second-order curve fitting, Eq. 3.2.25 with a constant offset is the "1/((1/a)+bx) + c" option:

1/((1/a)+bx) + c corresponds to $\left(\dfrac{1}{\dfrac{1}{A_o} + k_2\, t}\right) + A_\infty$

The fit values and correlations for the first-order plot are:

Fitting Function: a exp(-bx) + c
a= 1.1518 +- 0.0027
b= 0.2902 +- 0.0019
c= 0.046 +- 0.0019

sum of squared residuals= 0.0000436
stand. dev. y values= 0.002696
correlation between a & b= -0.1142
correlation between b & c= 0.7782
correlation between a & c= -0.503

The fit lines for both first and second order are shown in Figure 3.2.6.

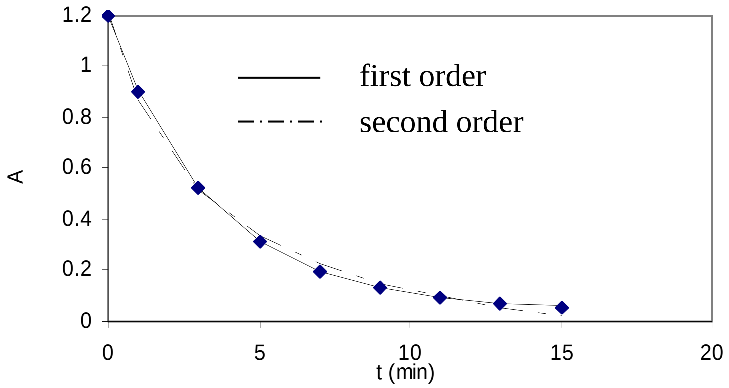


Figure 3.2.6: First and second-order nonlinear curve fits.

The first-order plot fits the experimental data over the complete time course, while the second-order fit is first below, then above, and finally below the data points. In other words, the second-order fit shows systematic deviations from the data (see Example 3.2.1). The standard deviation of the y values is a measure of the error of the data points above and below the fit values. The value of 0.002696 for the first-order plot is quite small. The standard deviation of the y values for the second-order plot, at 0.0255, is almost ten times larger, which agrees with our visual inspection. The correlation of the b and c fit values corresponds to the correlation of k and A_∞. This value of 0.7782 for the first-order plot shows the fit to be excellent with only moderate interaction between the values of the fit parameters.

Example 3.2.3: *Half-time Method*

The gas phase decomposition of acetaldehyde:

$CH_3CH{=}O\ (g) \rightarrow\ CH_4\ (g) + C{\equiv}O\ (g)$

has a half-time of 410. s for an initial pressure of 0.482 bar and 880. s for an initial pressure of 0.225 bar at 518°C. What is the order and rate constant for the reaction?

Answer: The reaction changes with initial partial pressure, so the reaction cannot be first order. Using Eq. 3.2.29, the rate constants for both initial conditions are calculated. If the rate constant is identical, to with in experimental error, then the reaction is determined to be second-order. For the initial pressure at 0.482 bar:

$$t_{½} = \frac{1}{P_{Ao}k_2} \ \text{ giving } \qquad k_2 = \frac{1}{P_{Ao}t_{½}} = \frac{1}{0.482\text{ bar }(410.\text{ s})} = 5.06\text{x}10^{-3}\text{ bar}^{-1}\text{ s}^{-1}$$

For the initial pressure at 0.225 bar:

$$k_2 = \frac{1}{P_{Ao}t_{½}} = \frac{1}{0.225\text{ bar }(880.\text{ s})} = 5.05\text{x}10^{-3}\text{ bar}^{-1}\text{ s}^{-1}$$

The results are identical within experimental error. The reaction is second order.

Example 3.2.4: *Zeroth-Order Integrated Rate Law*

Find the integrated rate law for a zeroth-order reaction. What linear form plot would you use to verify zeroth-order behavior? What is the half-time for a zeroth order reaction in terms of the rate constant?

Answer: A zeroth-order rate law is in the form: $-\frac{d[A]}{dt} = k$

The separation of variables gives: $d[A] = -\, k\, dt$

The indefinite integral is: $\int d[A] = -\int k\, dt$

or: $[A] = -\, k\, t + c$

Setting the boundary condition at time t = 0 as $[A] = [A]_o$ gives the integration constant as:

$[A]_o = c$

which upon substitution back into the integrated rate law gives:

$[A] = -\, kt + [A]_o$

A plot of [A] versus t gives a straight line with slope = – k. This integrated rate law is often rearranged to give: $[A] - [A]_o = -\, kt$. The half-time is when $[A] = [A]_o/2$:

$[A]_o/2 - [A]_o = -\, k\, t_{½}$

Solving for the half-time gives: $t_{½} = \frac{[A]_o}{2\,k}$

so the half-time is directly proportional to the initial concentration.

2nd Order – Two Reactants: Consider a reaction with two reactants that is first order with respect to each reactant:

$$A + B \rightarrow \text{products} \qquad 3.2.43$$

with the rate law:

$$-\frac{d[A]}{dt} = k_2 [A] [B] \qquad 3.2.44$$

Integrating Eq. 3.2.44 is a little more difficult because both [A] and [B] change with time. The concentrations of A and B are not independent; they both change by the same amount. In terms of the extent of the reaction, ξ/V, at $t = 0$, no reaction has taken place and $\xi/V = 0$. To make the equation a little easier to read, notice that concentrations are intensive and therefore are independent of the total volume. So we can assume $V = 1$ without loss of generality. From the 1:1 stoichiometry at time t:

$$[A] = [A]_o - \xi \qquad \text{and} \qquad [B] = [B]_o - \xi \qquad 3.2.45$$

Taking the derivative of $[A] = [A]_o - \xi$ to find the rate of disappearance of A gives:

$$-\frac{d[A]}{dt} = -\frac{d([A]_o - \xi)}{dt} = \frac{d\xi}{dt} \qquad 3.2.46$$

since $[A]_o$ is a constant. This last equation is a consequence of Eq. 3.1.6. Substitution of this last equation and Eqs. 3.2.45 into the original rate law, Eq. 3.2.44, gives:

$$\frac{d\xi}{dt} = k_2 ([A]_o - \xi) ([B]_o - \xi) \qquad 3.2.47$$

This equation is now easy to integrate because it only has one concentration variable, ξ. To separate the variables, both sides of the last equation are divided by $([A]_o - \xi)([B]_o - \xi)$ and multiplied by dt:

$$\frac{d\xi}{([A]_o - \xi)([B]_o - \xi)} = k_2 dt \qquad 3.2.48$$

Extensive tabulations of integrals can be found in standard references, such as the *CRC Handbook of Chemistry and Physics* or *Lange's Handbook*.[3-4] Many tables can also be found on-line. Take a moment soon to find sources that are convenient for you. Using one of these references will save time when doing homework. You might also use a computer based algebra program like *Maple* or *Mathematica*, which can do the harder integrals and algebraic manipulations in chemical kinetics. Using an integral table we find:

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a} \ln\left(\frac{b-x}{a-x}\right) \qquad 3.2.49$$

Using this standard integral gives the indefinite integrals of Eq. 3.2.48 as:

$$\frac{1}{[B]_o - [A]_o} \ln\left(\frac{[B]_o - \xi}{[A]_o - \xi}\right) = k_2 t + c \qquad 3.2.50$$

To find the integration constant we apply the boundary condition: $t = 0$, $\xi = 0$:

$$c = \frac{1}{[B]_o - [A]_o} \ln\left(\frac{[B]_o}{[A]_o}\right) \qquad 3.2.51$$

Substitution of the integration constant back into Eq. 3.2.50 gives the final result:

$$\frac{1}{[B]_o - [A]_o} \ln\left(\frac{[B]_o - \xi}{[A]_o - \xi}\right) = k_2 t + \frac{1}{[B]_o - [A]_o} \ln\left(\frac{[B]_o}{[A]_o}\right) \qquad 3.2.52$$

This equation is again in the form of a straight line. We can verify second-order behavior if a plot of the experimental data with the left-hand side of Eq. 3.2.52 as the vertical axis versus t gives a straight line with slope m = k_2, Figure 3.2.7.

Eq. 3.2.52 is often rearranged by subtracting the integration constant from both sides of the equation to give a form that can be compared to Eq. 3.2.5 for a first-order reaction and Eq. 3.2.27 for a single-reactant second-order reaction:

$$\frac{1}{[B]_o - [A]_o} \ln\left(\frac{[B]_o - \xi}{[A]_o - \xi}\right) - \frac{1}{[B]_o - [A]_o} \ln\left(\frac{[B]_o}{[A]_o}\right) = k_2 t \qquad 3.2.53$$

Combining the ln terms gives:

$$\frac{1}{[B]_o - [A]_o} \ln\left(\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - \xi)}\right) = k_2 t \qquad 3.2.54$$

If the initial concentrations of A and B are equal, Eqs. 3.2.52-54 are not applicable. Instead if $[A]_o = [B]_o$, then [A] = [B] during the course of the reaction and the integrated rate law is equivalent to Eqs. 3.2.25-3.2.27.

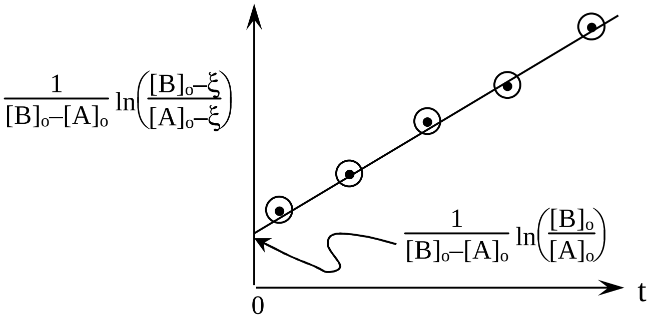


Figure 3.2.7: Second-order A + B → P kinetics: A linear plot of the left-hand side of Eq. 3.2.52 vs. t verifies first-order behavior with respect to each reactant.

Example 3.2.5: *Integrated Rate Law for A + B*

The hydrolysis of ethylacetate by sodium hydroxide has the following time course for a reaction with initial concentration of hydroxide of 0.0100 M and initial ethylacetate at 0.02656 M. This kind of reaction is called saponification:

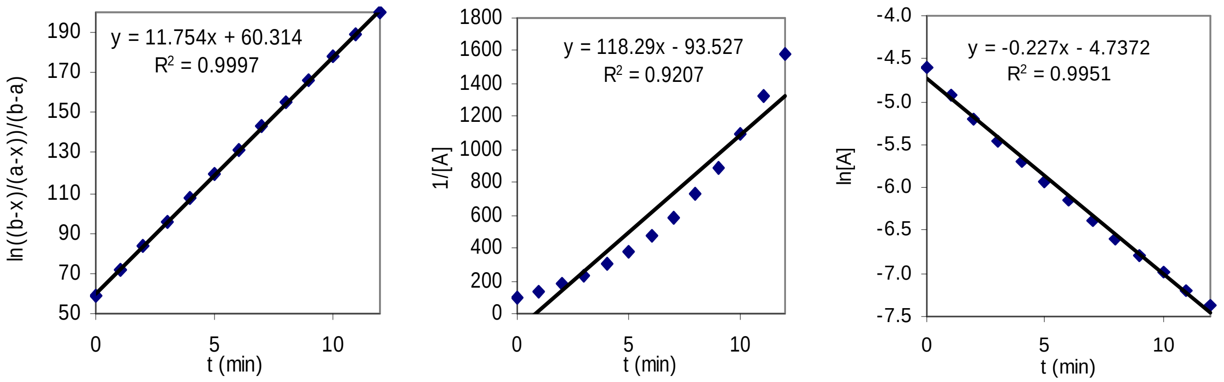
$$CH_3COOCH_2CH_3 + OH^- \rightarrow CH_3COO^- + CH_2CH_3OH$$

Saponification is the basis for the production of soap. The time course was determined using conductivity. Verify that the reaction is first order with respect to hydroxide, first order with respect to ethylacetate, and second order overall.

t (min)	0	1	2	3	4	5	6
$[OH^-]/10^{-3}$ M	10.000	7.307	5.467	4.285	3.348	2.634	2.133
t (min)	7	8	9	10	11	12	
$[OH^-]/10^{-3}$ M	1.698	1.361	1.131	0.918	0.754	0.630	

Answer: We need to do plots according to Eqs. 3.2.7, 3.2.27, and 3.2.52. The following spreadsheet was set up. Assume [A] is $[OH^-]$. Then $[A]_o = [OH^-]_o = 0.0100$ M and $[B]_o = 0.02656$ M. To calculate ξ in Eq. 3.2.52, note that $[OH^-] = [A]_o - \xi$, so $\xi = [OH^-]_o - [OH^-]$. The column labeled LHS is given by the left-hand side of Eq. 3.2.52 and is the vertical axis of Figure 3.2.8a.

t (min)	$[OH^-]$ (M)	x (M)	LHS	$1/[OH^-]$	ln $[OH^-]$
0	0.01	0.00000	58.990	100.000	-4.605
1	0.007307	0.00269	71.484	136.864	-4.919
2	0.005467	0.00453	84.156	182.914	-5.209
3	0.004285	0.00572	95.542	233.395	-5.453
4	0.003348	0.00665	107.655	298.644	-5.699
5	0.002634	0.00737	119.942	379.647	-5.939
6	0.002133	0.00787	131.084	468.799	-6.150
7	0.001698	0.00830	143.442	588.960	-6.378
8	0.001361	0.00864	155.668	734.664	-6.599
9	0.001131	0.00887	166.061	883.946	-6.784
10	0.000918	0.00908	177.961	1089.612	-6.994
11	0.000754	0.00925	189.299	1327.101	-7.191
12	0.00063	0.00937	199.644	1586.346	-7.369



(a) 2nd Order: A+B→ P (b) 2nd Order: A→ P (c) 1st Order: A→ P

Figure 3.2.8: Kinetic plots for the saponification of ethylacetate.

Figure 3.2.8a, shows that the reaction is first order in both reactants. Figure 3.2.8b rules out second-order behavior for OH^- and zeroth order for ethylacetate. Figure 3.2.8c, based on Eq. 3.2.7, rules out first-order behavior for OH^- and zeroth-order for ethylacetate. This last plot, even though it has an R^2 close to one, shows systematic curvature over the entire time course.

Example 3.2.6: *Second Order Rate Law in Terms of Extent*
Find the integrated rate law for an A → P second-order process using the form $[A] = [A]_o - \xi$. In other words, rederive Eq. 3.2.25 using the style of Eq. 3.2.47 with the extent of the reaction, ξ, as the independent composition variable.

Answer: The rate law is:

$$-\frac{d[A]}{dt} = k_2\,[A]^2 \qquad \text{or} \qquad \frac{d\xi}{dt} = k_2\,([A]_o - \xi)^2 \tag{3.2.55}$$

We can separate the variables by multiplying both sides of the equation by dt and dividing both sides of the equation by $([A]_o - \xi)^2$:

$$\frac{1}{([A]_o - \xi)^2}\,d\xi = k_2\,dt \tag{3.2.56}$$

The integral on the left is (see addendum 1.5, Table 1.5.1, or standard reference tables):

$$\int \frac{1}{(a-x)^2}\,dx = \frac{1}{(a-x)} + c' \tag{3.2.57}$$

Taking the indefinite integral of both sides and combining the integration constants gives:

$$\frac{1}{([A]_o - \xi)} = k_2\,t + c \tag{3.2.58}$$

To calculate the integration constant, we apply the boundary condition, at $t = 0$ then $\xi = 0$, giving $c = 1/[A]_o$. Substituting this value for the integration constant back into Eq. 3.2.58 gives the integrated rate law:

$$\frac{1}{[A]_o - \xi} = k_2\,t + \frac{1}{[A]_o} \tag{3.2.59}$$

which rearranges to a form commonly seen in the literature:

$$\frac{\xi}{[A]_o([A]_o - \xi)} = k_2 t \tag{3.2.60}$$

3.3 The Differential Method is Based Directly on the Rate Law

The integral method requires that we make assumptions about the order of the reaction and then compare the time course to the corresponding integrated rate laws. Differential methods calculate the order of the reaction directly from the data. Differential methods work with reactions of any order, including fractional orders.

Initial Rate Determinations: The differential method is a group of techniques that are based on measurements of the average rate of the reaction, Eq. 3.1.7. One group of techniques is based on determinations of the initial rate of the reaction. As we saw in section 1.3, general pattern ***℘1***, the short-time limiting behavior of an exponential function is approximately linear. Consider a general reaction with rate law given by $\upsilon = k\,[A]^n[B]^m$. Calculations of the initial rate using Eq. 3.1.7 for short times gives a constant value as long as $[A] \approx [A]_o$ and $[B] \approx [B]_o$. Then for two separate experiments with initial rates $\upsilon_{o,1}$ and $\upsilon_{o,2}$ with different values of the initial concentrations, $[A]_{o1}$ and $[A]_{o2}$, the rate laws are:

$$\upsilon_{o2} = k\,[A]_{o2}^n[B]_o^m \qquad 3.3.1$$
$$\upsilon_{o1} = k\,[A]_{o1}^n[B]_o^m \qquad 3.3.2$$

keeping $[B]_o$ the same for both reactions. The ratio of Eq. 3.3.1 to 3.3.2 gives:

$$\frac{\upsilon_{o2}}{\upsilon_{o1}} = \left(\frac{[A]_{o2}}{[A]_{o1}}\right)^n \qquad 3.3.3$$

Taking the ln of both sides of the last equation gives:

$$\ln\left(\frac{\upsilon_{o2}}{\upsilon_{o1}}\right) = n\,\ln\left(\frac{[A]_{o2}}{[A]_{o1}}\right) \qquad 3.3.4$$

which allows the calculation of the order of the reaction with respect to A. Initial rate studies require several kinetic runs, which requires extra time and reagents. The same information can be extracted from a single time course.

The Rate as a Function of the Concentration from the Time Course: The rate is a function of the concentration of each reactant during the time course of a single experiment. During the course of the reaction, taking the ln of both sides of $\upsilon = k\,[A]^n[B]^m$ gives:

$$\ln \upsilon = n \ln[A] + \ln(k\,[B]^m) \qquad 3.3.5$$

If we use the isolation method by keeping [B] in large excess, then $[B] \approx [B]_o$ and a plot of $\ln \upsilon$ versus ln[A] gives a straight line with slope n. We often use the average rate instead of the instantaneous rate and then the corresponding concentration should be the average concentration during the time interval of each data point, Eq. 3.1.7.

The integral and half-time methods are usually sufficient for reactions where the concentration of a reactant or product can be calculated with good precision from the analytical method. However, we often work with absorbance or conductivity directly instead of concentrations, as in Eq. 3.2.36-41. There may be significant uncertainty in the limiting values at time zero and at long times. Uncertainty in the values of A_o and A_∞ can cause significant curvature in the linear form of kinetic plots, Figures 3.2.1 and 3.2.3, and cause incorrect conclusions about the order of the reaction. Differential methods are somewhat less susceptible to uncertainty in the limiting values.

Example 3.3.1: *The Differential Method*

Denitrification is the reduction of either nitrate (NO_3^-) or nitrite (NO_2^-) to the gaseous oxides or N_2 by aerobic bacteria. Bacteria capable of reducing nitrate to N_2 typically dominate in ground water. Denitrification of ground water can be represented by the reaction sequence:

$$NO_3^- \rightarrow NO_2^- \rightarrow \tfrac{1}{2} N_2$$

The reaction order with respect to nitrate has been reported to be half-order on the basis of theoretical considerations.[6] The following data was taken on the nitrate levels in a biofilm-based reactor. Determine the order of the reaction using the differential method.

t (hr)	0	0.49	1.19	1.70
$[NO_3^-]$ (mg L^{-1})	409.0	178.2	23.8	0.0

Answer: Using Eq. 3.1.7 the average rate for each successive interval can be calculated. For example, for the first interval:

$$\bar{\upsilon} = -\frac{c_i(t_2) - c_i(t_1)}{t_2 - t_1} = -\frac{178.2 - 409.0}{0.49 - 0} = 471.0 \text{ mg L}^{-1} \text{ hr}^{-1}$$

and the concentration in the middle of this first time interval is:

$$\bar{c} = \frac{c_i(t_1) + c_i(t_2)}{2} = \frac{178.2 + 409.0}{2} = 293.6 \text{ mg L}^{-1}$$

A spreadsheet was constructed with rates and average nitrate concentrations, as shown below. The ln of the average nitrate concentration and the ln of the rate are also included.

t (hr)	[NO3$^-$]	$\bar{c}$ = [NO3$^-$](av)	$\bar{\upsilon}$ = rate (av)	ln [NO3$^-$] (av)	ln rate
0	409.0				
0.49	178.2	293.6	471.0204	5.6822	6.1549
1.19	23.8	101	220.5714	4.6151	5.3962
1.7	0.0	11.9	46.66667	2.4765	3.8430

The plot of ln $\bar{\upsilon}$ versus ln $\bar{c}$ is shown below. The slope of the line is close to 0.75 or ¾. The uncertainty can't be statistically evaluated with so few points.

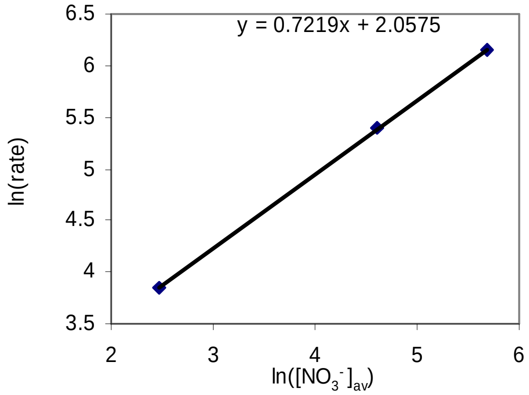


Figure 3.3.1: Differential method applied to aerobic denitrifcation using a biofilm.

For this data set, the apparent order is about ¾. More data points are necessary to get a better plot for comparison to the expected value of ½. See Problem 18 for time course comparisons.

3.4 Progress Towards Equilibrium

No reaction goes to completion. Even for the most thermodynamically favorable reactions, small amounts of reactants remain at the end of the reaction. The integrated rate laws we have derived so far neglect this possibility. We first consider the general case and then consider the integrated rate law for a reversible first-order reaction. The concept of chemical equilibrium flows naturally from these considerations.

Opposed Reactions: Consider a reaction that is **reversible**. That is, the forward and reverse reactions are considered with k_f the rate constant for the forward direction and k_r the rate constant for the reverse reaction:

$$\mathrm{A + B} \underset{k_r}{\overset{k_f}{\rightleftarrows}} \mathrm{C + D} \tag{3.4.1}$$

This reaction scheme could also have been written in the following equivalent way:

$$\mathrm{A + B} \xrightarrow{k_f} \mathrm{C + D} \tag{3.4.2}$$

$$\mathrm{C + D} \xrightarrow{k_r} \mathrm{A + B} \tag{3.4.3}$$

The combination of the two steps is often called an **opposed** reaction mechanism. The choice of expressing the reaction scheme by Eq. 3.4.1 or 3.4.2 and 3.4.3 is by convenience, whichever helps you to see the overall relationships. Assume that the rate law for the forward reaction, Eq. 3.4.2, is first order in both A and B:

$$\text{forward rate} = \upsilon_+ = k_f\,[\mathrm{A}]\,[\mathrm{B}] \tag{3.4.4}$$

In addition, assume that the reverse reaction, Eq. 3.4.3, is also first order in C and D:

$$\text{reverse rate} = \upsilon_- = k_r\,[\mathrm{C}]\,[\mathrm{D}] \tag{3.4.5}$$

The net rate of change of A is the difference of these changes; the forward rate decreases A and the reverse rate increases A:

$$-\frac{d[\mathrm{A}]}{dt} = k_f\,[\mathrm{A}]\,[\mathrm{B}] - k_r\,[\mathrm{C}]\,[\mathrm{D}] \tag{3.4.6}$$

At the beginning of the reaction, [C] and [D] are small and the rate law reduces to Eq. 3.2.31. As the reaction progresses [C] and [D] increase and [A] and [B] decrease until the rate of change of A goes to zero:

$$-\frac{d[\mathrm{A}]}{dt} = k_f\,[\mathrm{A}]\,[\mathrm{B}] - k_r\,[\mathrm{C}]\,[\mathrm{D}] = 0 \qquad \text{(equilibrium)} \tag{3.4.7}$$

At this point, the reaction shows no further tendency for change and the concentrations of all the reactants and products remain constant in time. When the concentrations remain constant, the system is at **equilibrium**. Rearranging Eq. 3.4.7 at equilibrium gives:

$$k_f\,[\mathrm{A}]\,[\mathrm{B}] = k_r\,[\mathrm{C}]\,[\mathrm{D}] \qquad \text{(equilibrium)} \tag{3.4.8}$$

which from Eqs. 3.4.4 and 3.4.5 shows that the forward and reverse rates for the reaction are equal at equilibrium:

$$\text{forward rate} = \text{reverse rate} \quad \text{or} \quad \upsilon_+ = \upsilon_- \qquad \text{(equilibrium)} \qquad 3.4.9$$

Solving for the ratio of the rate constants gives the equilibrium ratio of the concentrations:

$$\frac{k_f}{k_r} = \left(\frac{[C]\,[D]}{[A]\,[B]}\right)_{eq} \qquad \text{(equilibrium)} \qquad 3.4.10$$

This ratio is constant for any initial mixture of [A] and [B] once the system attains equilibrium. The ratio of the forward and reverse rate constants is defined as the **equilibrium constant** K_{eq}:

$$K_{eq} \equiv \frac{k_f}{k_r} = \left(\frac{[C]\,[D]}{[A]\,[B]}\right)_{eq} \qquad \text{(equilibrium)} \qquad 3.4.11$$

When the equilibrium constant is expressed in terms of concentrations, as it is in this last equation, the symbol K_c is often adopted. For gas phase reactions, the rate law and the corresponding equilibrium ratio can also be expressed in partial pressures, in which case the equilibrium constant is denoted K_p. The equilibrium state is the final resting point for the chemical reaction; in other words, the equilibrium constant determines how far the reaction runs towards products. This relationship among the forward and reverse rate constants and the equilibrium constant is a central focal point for much of the rest of this text.

The concept of a reversible chemical reaction is distinct from the thermodynamic concept of reversibility that we introduced in Chapter 1. A reversible reaction from a kinetic standpoint just means the reaction runs forwards and backwards. Thermodynamic reversibility for a chemical reaction requires kinetic reversibility and that the reaction is also at equilibrium. From a thermodynamic perspective, the equations that we have derived in this chapter describe the irreversible progress towards equilibrium. We will have much more to say about the relationship of kinetics to equilibrium in the next chapter. For now we focus on the time course for the reaction as it approaches equilibrium.

Opposed, First Order: The rate law for an opposed reaction depends on the reaction orders and the stoichiometry. Consider a first-order forward reaction and first-order reverse reaction as a simple example:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \qquad 3.4.12$$

Where k_1 is the rate constant for the forward reaction and k_{-1} is for the reverse reaction. The corresponding rate law with the assumed reaction orders is:

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B] \qquad 3.4.13$$

To integrate this rate law, we need to relate the concentrations of the reactant and product during the course of the reaction. Initially, assume $[A] = [A]_o$ and $[B] = 0$. As the reaction progresses, from the stoichiometry, $[B] = [A]_o - [A]$. At equilibrium, $[A] = [A]_{eq}$ and $[B]_{eq} = [A]_o - [A]_{eq}$. These relationships are summarized in the following table.

Table 3.4.1: Concentrations for an opposed first-order/first-order reaction.

Progress	[A]	[B]
initial	$[A]_o$	0
middle	[A]	$[B] = [A]_o – [A]$
equilibrium	$[A]_{eq}$	$[B]_{eq} = [A]_o – [A]_{eq}$
displacement	$[A] – [A]_{eq}$	$[B] – [B]_{eq} = [A]_{eq} – [A]$

The **displacement** away from equilibrium for A is defined as $[A] – [A]_{eq}$. The displacement for B is calculated by taking the difference of the corresponding rows in Table 3.4.1:

$$[B] – [B]_{eq} = [A]_{eq} – [A] = – ([A] – [A]_{eq}) \qquad 3.4.14$$

If [A] is larger than its equilibrium value then [B] must be smaller than its equilibrium value by the same amount, because of the 1:1 stoichiometry. At equilibrium the rate of change of A is zero giving Eq. 3.4.13 as:

$$k_1[A]_{eq} – k_{-1}[B]_{eq} = 0 \qquad \text{(equilibrium)} \quad 3.4.15$$

The equilibrium constant determines the ratios of the products to reactants:

$$\frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}} \qquad \text{(equilibrium)} \quad 3.4.16$$

The rate law is expressed in terms of the displacement by subtracting Eq. 3.4.15 from Eq. 3.4.13:

$$– \frac{d[A]}{dt} = k_1[A] – k_1[A]_{eq} – k_{-1}[B] + k_{-1}[B]_{eq} \qquad 3.4.17$$

Distributing out the rate constants gives:

$$– \frac{d[A]}{dt} = k_1([A] – [A]_{eq}) + k_{-1}(– [B] + [B]_{eq}) \qquad 3.4.18$$

Using Eq. 3.4.14 to relate the displacement in B to the displacement in A in the second term gives:

$$– \frac{d[A]}{dt} = k_1([A] – [A]_{eq}) + k_{-1}([A] – [A]_{eq}) \qquad 3.4.19$$

Distributing out the displacement gives the much simpler relationship:

$$\frac{d[A]}{dt} = – (k_1 + k_{-1})([A] – [A]_{eq}) \qquad 3.4.20$$

However, $d([A]–[A]_{eq})/dt = d[A]dt$, since $[A]_{eq}$ is a constant. Then Eq. 3.4.20 can be rewritten:

$$\frac{d([A] – [A]_{eq})}{dt} = – (k_1 + k_{-1})([A] – [A]_{eq}) \qquad 3.4.21$$

Eq. 3.4.21 is a *simple exponential process* and by general pattern $\wp$ ***1*** with lower integration limit $[A] = [A]_o$ at $t = 0$:

$$\int_{[A]_o}^{[A]} \frac{d([A]-[A]_{eq})}{([A]-[A]_{eq})} = -\int_0^t (k_1 + k_{-1})\, dt \qquad 3.4.22$$

giving $$\ln\left(\frac{[A]-[A]_{eq}}{[A]_o-[A]_{eq}}\right) = -(k_1 + k_{-1})\, t \qquad 3.4.23$$

This last equation looks a bit complicated. However, if the reaction did run to completion, the equilibrium value of A would be $[A]_{eq} = 0$, there would be no reverse reaction, and Eq. 3.4.24 reduces to Eq. 3.2.5. To verify this integrated rate law, a plot of $\ln(([A]-[A]_{eq})/([A]_o-[A]_{eq}))$ versus t gives a straight line with slope = $-(k_1 + k_{-1})$. In other words, you just need to subtract the equilibrium concentration from the numerator and denominator of Eq. 3.2.4. The time course is obtained by solving for [A]:

$$[A] = ([A]_o - [A]_{eq})\, e^{-(k_1+k_{-1})t} + [A]_{eq} \qquad 3.4.24$$

Note the limiting behavior of this last equation. When t = 0 then $e^{-(k_1+k_{-1})t} = 1$, and $[A] = [A]_o$. When $t \rightarrow \infty$ then $e^{-(k_1+k_{-1})t} \rightarrow 0$, and $[A] = [A]_{eq}$. Figure 3.4.1 shows the time course for a reaction that approaches equilibrium compared to a reaction that goes to completion.

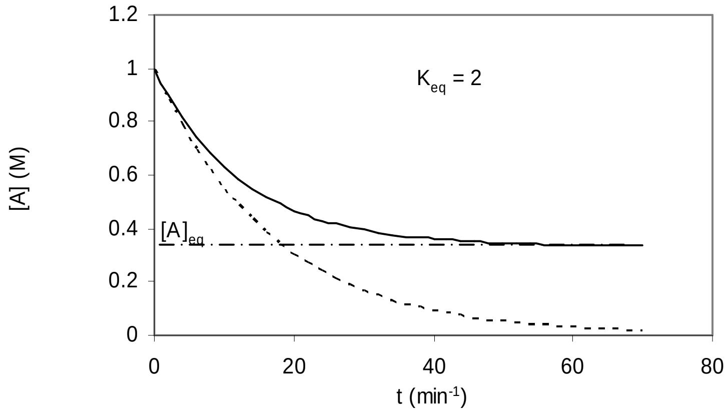


Figure 3.4.1: Comparison of a reaction that goes to equilibrium (solid line) compared to a reaction that runs to completion (dashed line).

The limiting slope at t = 0 is $-([A]_o - [A]_{eq})(k_1 + k_{-1})$, so the initial rate is proportional to the sum of the forward and reverse rate constants.

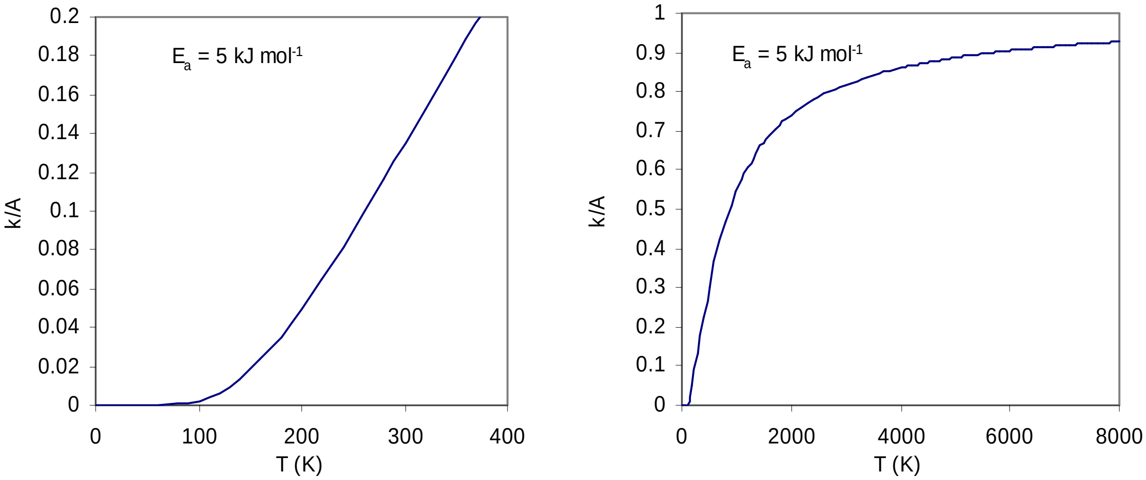
After the rate law for the reaction is determined, we move to stage 2, where possible mechanisms are proposed. However, before going on to study mechanisms, we should take a careful look at the temperature dependence of reaction rates.

3.5 Temperature Dependence of Reaction Rates

A typical chemical reaction roughly doubles in rate for every 10 K temperature increase near room temperature.[7] After the study of the temperature dependence of a variety of chemical reactions, Svante Arrhenius, in 1889, empirically determined that the rate constants for a majority of reactions followed the relationship:

$$k = A\, e^{-E_a/RT} \qquad 3.5.1$$

where A is the pre-exponential factor and E_a is the activation energy. Eq. 3.5.1 is one expression of the **Arrhenius equation**. The activation energy is a measure of the collision energy necessary for the bond breaking and making steps to occur. The pre-exponential factor is the product of the rate of intermolecular collisions and a probability factor that depends on the collision geometry and timing. In solution, it is better to talk about molecular encounters rather than collisions, but the minimum energy requirement still applies. In solution, the solvent can act as a cage surrounding both reactants so that many collisions occur when the reactants approach each other at short range. The activation energy is usually large and positive. However, some reactions, such as ion-molecule reactions, have no activation energy. Some reactions have negative activation energies; that is, the reactions slow with temperature increase. The "chemist's rule" that the reaction rate doubles for every 10 K temperature increase corresponds to an activation energy of about 50 kJ mol^{-1}. In the ratio E_a/RT, the RT term is a measure of the available thermal kinetic energy through collisions. At room temperature RT is about 2.5 kJ mol^{-1}, which is much less than the typical activation energy.



(a) (b)

Figure 3.5.1: Arrhenius temperature dependence in the (a) low temperature and (b) high temperature regions. An unusually small E_a of 5 kJ mol^{-1} was chosen to facilitate displaying both plots. The vertical axis is the rate constant divided by the pre-exponential factor.

A plot of the Arrhenius equation for low temperatures that correspond to $RT \ll E_a$ produces a rapidly increasing temperature dependence, Figure 3.5.1a. For much higher temperatures, the rate constant approaches a maximum equal to the pre-exponential factor, Figure 3.5.1b. For most reactions, the high temperature region is not accessible, except in high temperature flames, lightning strikes, or atmospheric reactions in the thermosphere (1000-1500 K).

Finding A and E_a from experimental data by non-linear curve fitting to Eq. 3.5.1 is straightforward, and in many ways preferable. However, Eq. 3.5.1 is usually recast into linear form. The best linear method to use depends on the number of available data points. If many data points are available, the Arrhenius equation is recast into a straight line form that is convenient for linear curve fitting. Taking the ln of both sides of Eq. 3.5.1 gives:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad 3.5.3$$

A plot of the ln k versus 1/T gives a straight line with slope $-E_a/R$ and intercept ln A, Figure 3.5.2. If only two data points are available an alternate form is better.

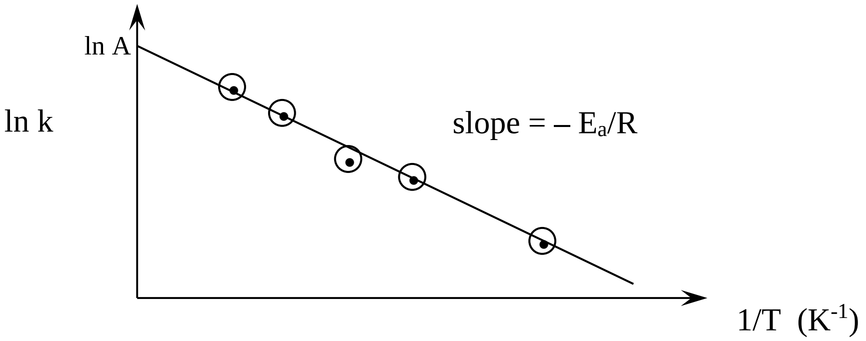


Figure 3.5.2: Arrhenius behavior is verified by plotting ln k versus 1/T. This plot is often called an Arrhenius plot or an activation energy plot. The intercept is usually extrapolated well beyond the range of observations making the uncertainty in A quite large.

Assume that the rate constant for the reaction is known only at two different temperatures, k_{T1} and k_{T2} at T_1 and T_2, respectively. Evaluating Eq. 3.5.3 for these two data points gives:

$$\ln k_{T2} = \ln A - \frac{E_a}{RT_2} \qquad 3.5.4$$

$$\ln k_{T1} = \ln A - \frac{E_a}{RT_1} \qquad 3.5.5$$

Subtracting the last two equations gives:

$$\ln k_{T2} - \ln k_{T1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad 3.5.6$$

The difference in the ln terms is the ln of the ratio:

$$\ln \frac{k_{T2}}{k_{T1}} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad 3.5.7$$

This form of the Arrhenius equation for two data points is a very common functional form. We will encounter this general form when we consider the temperature dependence of equilibrium constants and colligative properties.

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General Pattern 4: Exponential Temperature Dependence: $e^{-E/RT}$:

The exponential form of the temperature dependence in Eq. 3.5.1 appears in many different problems. The role of the activation energy can be replaced by other energy parameters including internal energy, enthalpy, and Gibbs energy, depending on the problem. The role of the rate constant can be replaced by equilibrium constants or concentrations for specific problems. The barometric formula, Eq. 1.3.16°, is another example. Using Arrhenius behavior as the example, the three equations:

$$k = A\, e^{-E_a/RT} \qquad \ln k = \ln A - \frac{E_a}{RT} \qquad \ln \frac{k_{T2}}{k_{T1}} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

are all equivalent. You should practice converting among the three forms. The ln based terms are in a linear form that is useful for linear curve fitting. Comparing Eq. 3.5.3 to the general equation for a straight line:

$$\begin{aligned} \ln k &= -\frac{E_a}{RT} + \ln A \\ y &= mx + b \end{aligned} \qquad 3.5.8$$

shows that associating 1/T with x gives the slope as $m = -E_a/R$ and the intercept as $b = \ln A$, Figure 3.5.2. Eq. 3.5.7 can also be rearranged to give linear form. Going back to Eq. 3.5.6 and solving for $\ln k_{T2}$ and grouping the terms in T_1 together on the right-side of the equation:

$$\begin{aligned} \ln k_{T2} &= -\frac{E_a}{R}\left(\frac{1}{T_2}\right) + \left(\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln k_{T1}\right) \\ y &= mx + b \end{aligned} \qquad 3.5.9$$

Once again, the slope of the straight line form is shown to be $m = -E_a/R$. The intercept involves only the initial data point. This intercept looks complicated and unusual. However, notice that solving Eq. 3.5.3 for ln A specifically at the temperature T_1 shows that the intercept for Eq. 3.5.9 is:

$$b = \left(\frac{E_a}{R}\left(\frac{1}{T_1}\right) + \ln k_{T1}\right) = \ln A \qquad 3.5.10$$

Once again the intercept is $b = \ln A$, as in Eq. 3.5.8. If you are given an equation in the form of Eq. 3.5.7 you should immediately be able to spot that a plot of ln k vs. 1/T will give a straight line of slope $-E_a/R$. Eq. 3.5.7 can also be solved for the rate constant, which is also a general form that is found in the literature:

$$k_{T2} = k_{T1}\, e^{\frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \qquad 3.5.11$$

Now consider the temperature dependence in Eq. 3.5.7 and 3.5.11. Please remember that:

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \neq \left(\frac{1}{T_2 - T_1}\right) \qquad \text{incorrect!!}$$

It is often just best to leave the temperature term in the form in Eq. 3.5.7. However, taking a common denominator can be useful:

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \left(\frac{T_1 - T_2}{T_1\, T_2}\right) = -\left(\frac{T_2 - T_1}{T_1\, T_2}\right) = -\left(\frac{\Delta T}{T_1\, T_2}\right) \qquad 3.5.12$$

where $\Delta T = T_2 - T_1$. Since the temperatures are often near 300 K, for narrow temperature ranges, it is often an acceptable approximation to let $T_1T_2 \approx T_1^2$ in the denominator and then:

$$\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \cong -\left(\frac{\Delta T}{T_1{}^2}\right) \qquad \text{(small } \Delta T\text{)} \qquad 3.5.13$$

Using this approximation, Eq. 3.5.7 becomes:

$$\ln\frac{k_{T2}}{k_{T1}} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \cong \frac{E_a}{RT_1{}^2}\,\Delta T \qquad \text{(small } \Delta T\text{)} \qquad 3.5.14$$

This approximation will be useful for colligative properties.

An exponentially increasing function of the form e^{cx} is a common occurrence, for example in exponential population growth. How similar are the forms e^{cx} and $e^{-c/x}$? Our current case of an activated chemical reaction is a good example. Over narrow temperature ranges for $RT \ll E_a$ the functional dependence for the rate constant looks a lot like a simple exponential process. Solving Eq. 3.5.14 for k_{T2} gives:

$$k_{T2} \cong k_{T1}\; e^{\left(\frac{E_a}{RT_1{}^2}\right)\Delta T} \qquad \text{(small } \Delta T\text{)} \qquad 3.5.15$$

which shows that the rate constant is approximately an exponentially increasing function of temperature, if the range of temperatures of interest is small and $RT \ll E_a$. A comparison of the exact form of the Arrhenius equation with the approximation in Eq. 3.5.15 is plotted in Figure 3.5.3, for $T_1 = 300$ K.

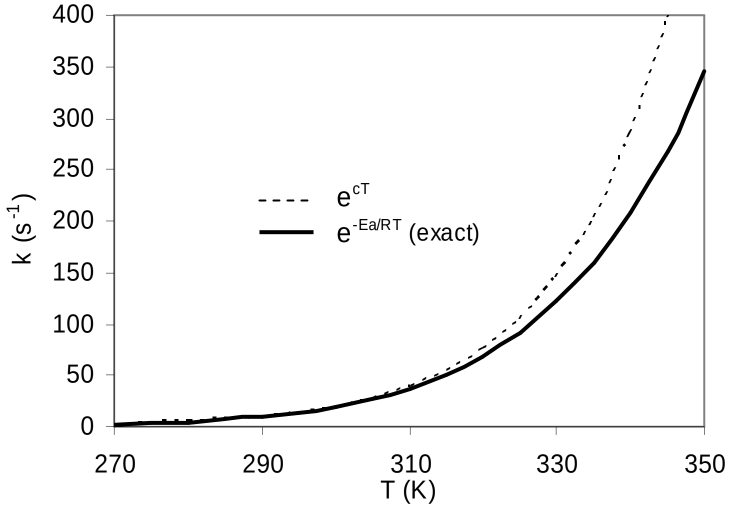

Figure 3.5.3: The Arrhenius temperature dependence, $e^{-Ea/RT}$, can be approximated as a simple exponential increase with temperature, e^{cT}, for narrow temperature ranges. The constant is $c = E_a/RT_1{}^2$. The temperature dependence for a simple exponential is stronger than for an activated process.

The "Chemists Rule" gives a constant factor increase in rate for every 10 K increase and corresponds to pure exponential behavior, Eq. 3.5.14. Figure 3.5.3 shows that the "Chemists Rule" holds for only a narrow temperature range, near T_1. When the activation energy is 50 kJ mol^{-1}, the "Chemists Rule" is applicable just near room temperature. Similar approximate doubling rules can be expressed for other examples of $e^{-E/RT}$ temperature dependence.

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Alternatives to Arrhenius Behavior: Some reactions do not follow the functional form of Eq. 3.5.1. The derivation of the Arrhenius equation from theoretical considerations is the topic of the chemical dynamics chapter later in this text. Some theories suggest that the temperature dependence is better expressed as:

$$k = a\, T^m\, e^{-E_a/RT} \qquad 3.5.19$$

where m = 1, 2, or ±½. Experimental values for m are often non-integer or negative. It is difficult experimentally to determine the value of m, and most reactions follow Eq. 3.5.1 over a useful temperature range.

Example 3.5.1: *Arrhenius Temperature Dependence*
The rate constant for the decomposition of N_2O_5 at 25.°C is $3.46\text{x}10^{-5}\ s^{-1}$ and at 65.°C is $4.87\text{x}10^{-3}\ s^{-1}$. Calculate the activation energy and the pre-exponential factor.

Answer: Absolute temperatures are necessary, which are 298.2 K and 338.2 K, respectively. Since only two data points are given, Eq. 3.5.7 is appropriate:

$$\ln \frac{k_{T2}}{k_{T1}} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{4.87\text{x}10^{-3}}{3.46\text{x}10^{-5}} = -\frac{E_a}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{338.2\ \text{K}} - \frac{1}{298.2\ \text{K}}\right)$$

$$4.9470 = -\frac{E_a}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}(-3.966\text{x}10^{-4})$$

[Hint on significant figures: To get a quick estimate of the number of significant figures in the ln term, just calculate $\ln(4.8\mathbf{8}\text{x}10^{-3}/3.46\text{x}10^{-5})$ or $\ln(4.87\text{x}10^{-3}/3.4\mathbf{7}\text{x}10^{-5})$ and notice how much the answer changes from the previous value with the constants given in the problem. You can also use the significant figure rule for ln to get the same result, Appendix 1.]

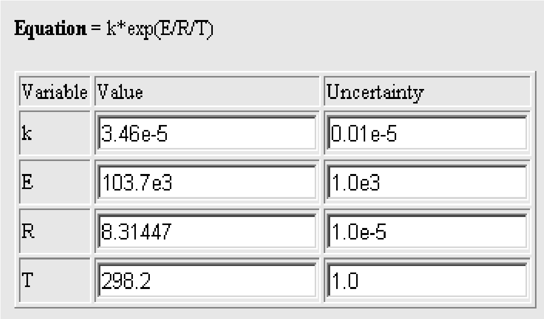
Solving for the activation energy gives E_a = 103.7 kJ mol^{-1}. We can then solve Eq. 3.5.1 using either temperature data point to determine the pre-exponential factor. Using the lower temperature gives:

$$k = A\, e^{-E_a/RT} = 3.46\text{x}10^{-5}\ s^{-1} = A\, e^{-103.7\text{x}10^{3}\ \text{J}/(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\ 298.2\ \text{K})}$$
$$3.46\text{x}10^{-5}\ s^{-1} = A\,(6.83\text{x}10^{-19})$$
$$A = 5.1\ \text{x}10^{13} \pm 2.2\text{x}10^{13}\ s^{-1}$$

www For the error analysis for the pre-exponential factor, we used the “Uncertainty Calculator” applet that is on the textbook Web site and on the text companion CD. To calculate the error in A, here’s how the values were entered:


Equation: k*exp(E/R/T)

After you click on Calculate, the following window appears:



Equation = k*exp(E/R/T)

Variable	Value	Uncertainty
k	3.46e-5	0.01e-5
E	103.7e3	1.0e3
R	8.31447	1.0e-5
T	298.2	1.0

Notice that you can click in a table cell and then press the Constants button to get a common list of fundamental constants and conversion factors with the literature uncertainties. The conclusion is that error propagation for exponentiation is often quite unfavorable.

3.6 Fast Reaction Techniques

Chemical reactions are often quite rapid and require specialized techniques to determine the time course. Table 3.6.1 outlines several useful techniques that we will discuss.

Table 3.6.1: Techniques for measuring the rates of chemical reactions.[8]

Method	Description	Timescale
Conventional	Mix reactants in a cuvette or beaker and monitor.	≥ 10 s
Stopped Flow	Mix reactants through jets in a small volume chamber using pneumatically driven syringes.	$\geq 10^{-1}$ s
Flash Photolysis: Laser Flash Photolysis, LFP	Starting at equilibrium, initiate a photochemical process by a short flash from a laser or xenon flash lamp.	10^{-9}-10^{-1}s
Chemical Relaxation: Temperature, Pressure, or Concentration Jump	Starting at equilibrium rapidly change the temperature, pressure, or a concentration to shift the position of equilibrium.	$\geq 10^{-6}$ s
NMR Chemical Exchange: Line broadening (see the magnetic resonance chapter)	Starting at equilibrium, monitor line broadening with changes in temperature or concentration.	10^{-2}-10^{-9} s

Stopped Flow: The limitation on determining the rate of a reaction is often simply the time it takes to mix the reactants together. Stopped flow is just a fancy way to rapidly and efficiently mix reactants in a small volume cell. The cell may be a cuvette for absorption or fluorescence, a cell for conductivity determinations, or a cell for magnetic resonance measurements like electron spin resonance (please see the magnetic resonance spectroscopy chapter). Other than the mixing speed, the time course is monitored conventionally, although with instruments that have a rapid time response. The minimum mixing times are on the order of 10 milliseconds. A diagram of a stopped flow accessory is shown in Figure 3.6.1.

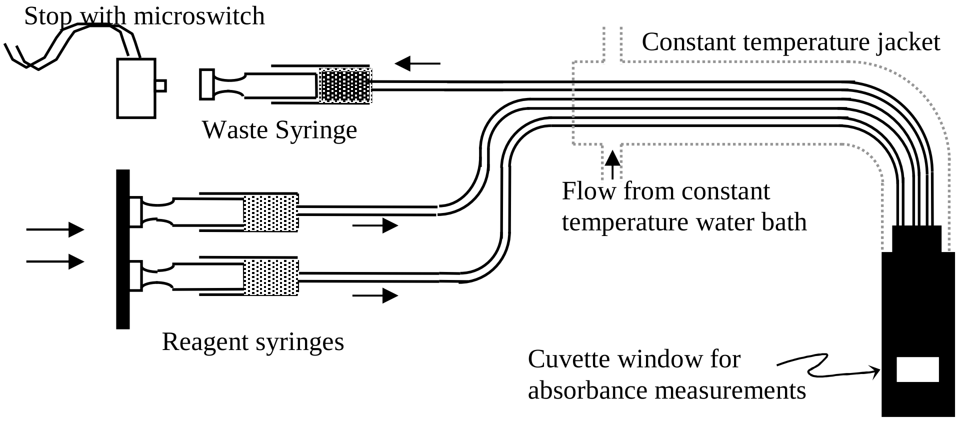


Figure 3.6.1: Stopped flow apparatus for rapid kinetics measurements. The reagents are rapidly mixed in a micro-volume spectrophotometer cuvette.

The reagents are placed in syringes. The syringes are connected to the flow-through cuvette with Teflon tubing. The cuvette has nozzles specifically designed to generate turbulence to enhance the mixing efficiency. The syringes are pushed either by hand or by computer-controlled pneumatic cylinders. The waste from the cuvette flows into a waste syringe. When the waste syringe fills, the barrel of the syringe contacts the stop block, which simultaneously stops the injection and contacts a switch that starts the data acquisition. In favorable circumstances, reaction half-times as short as 0.05 s are measurable. Stopped flow techniques are particularly useful for fast enzyme kinetics studies and observing free-radical intermediates in inorganic and environmental reactions.

Flash Photolysis: When stopped-flow mixing times are too slow, alternate techniques are required. The following techniques all start with the reaction mixture at equilibrium, which avoids the mixing time issue. Photochemical reactions can be studied by exciting the reaction mixture with ultra-short bursts of light from either a laser or a pulsed xenon flash lamp. The limiting factor in the minimum half-times that are observable is the temporal width of the excitation pulse. In general, the pulse width of the light source must be much shorter than the half-time of the chemical reaction. The pulse width of xenon flash lamps, such as those used in photography, is in the microsecond time scale. For faster reactions, specially designed lasers must be used that have pulse widths in the nanosecond range. Using ultra-fast pulsed lasers allows processes in the sub-femtosecond time scale to be studied. Readily available lasers have pulse widths in the 10 nanosecond range, allowing many photochemical processes to be studied.

One disadvantage of laser-driven systems is that ultraviolet lasers have a fixed wavelength. Several different types of lasers are often necessary to provide coverage of the UV range of common organic and inorganic reactants. Nd-YAG lasers and eximer lasers are commonly used. Nd-YAG is the acronym for a neodymium-yttrium aluminum garnet solid-state laser. Nd-YAG is a synthetic "mineral" that is excited by flash lamps to produce light at 1064 nm in the IR region of the spectrum. To convert the IR light into the visible and then the UV region, a special optical trick is used. Certain substances have non-linear optical properties in intense laser irradiation that combines the photons; doubling and then tripling and then quadupling the photon frequency are possible. Doubled output of a Nd-YAG laser is at 532 nm, which is in the green region of the spectrum. Tripled output is at 355 nm and quadrupled at 266 nm.

Eximer lasers use gas phase chemical reactions to produce highly excited diatomic molecules that emit light. The chemical reaction that drives the laser is initiated by an intense electrical discharge. The reaction used is normally between xenon and either fluorine or chlorine, producing either XeF or XeCl. The product is produced in a highly excited state with a lifetime in the nanosecond range. In returning to the ground state, light is emitted in a short pulse. XeCl provides laser emission at 308 nm with a pulse width of about 10 nsec.

Many different techniques are available for monitoring the progress of photochemical reactions. Conductivity, IR, Raman, mass spectrometry, and chemiluminescence are all used. However, the most commonly used technique is UV/Visible absorption spectrophotometry, Figure 3.6.2. The signal acquisition must be very fast. The signal from the photodetector is digitized using a very fast digital oscilloscope.

Flash photolysis is useful for photochemical reactions, but is not applicable to other types of reactions. Chemical relaxation techniques can be used more generally, but not with such short time resolution.

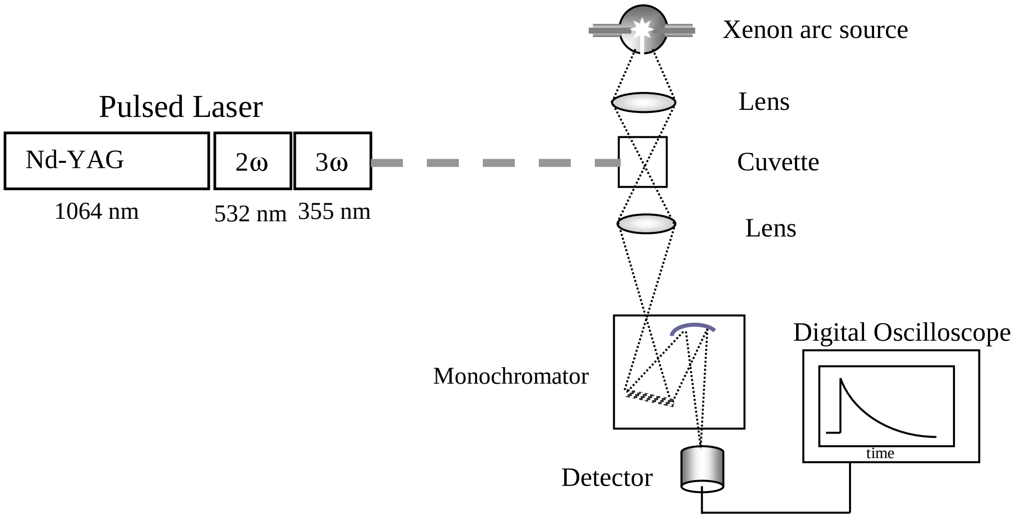


Figure 3.6.2: Laser flash photolysis, LFP, for photochemical reactions. A tripled Nd-YAG laser produces 10 ns pulses at 266 nm. The reaction is monitored using UV/Visible absorption and a fast digital oscilloscope. A xenon arc source is often used to provide intense UV and visible light for the monitoring beam. A photomultiplier with fast electronics is used as the detector.

Chemical Relaxation: Chemical relaxation techniques use a sudden perturbation in temperature, pressure, electric field, or concentration to shift the position of equilibrium for a reacting system. After the perturbation, the system is monitored as a function of time as the system approaches the new equilibrium position. The process of attaining the new equilibrium position is often called **chemical relaxation**. The limit for determining fast reaction rates is determined by the time necessary for the perturbation. Intense CO_2 lasers are available that can produce temperature jumps up to 6°C in a few microseconds.[8] Electric discharges through electrolyte solutions can also be used for temperature jumps by Joule heating. Specialized piezoelectric systems can provide pressure jumps of 100 bar in about 100 μs.[9] However, temperature jump experiments can also be done with simple apparatus. The cooling or heating water flowing through a jacketed spectrophotometer cuvette can be switched between two constant temperature baths at different temperatures. Chemical relaxation techniques are useful for enzyme kinetics experiments as well as inorganic ligand exchange and the kinetics of free radical intermediates.[8,10] Temperature and pressure jump techniques have become quite important in the study of protein folding.[9,11] Chemical relaxation is also an important part of the theory of irreversible thermodynamics (see Chapter 22).

The key result of chemical relaxation techniques is that all single-step chemical reactions, independent of the rate law, relax towards equilibrium by a first-order process that is characterized by a single relaxation time τ. This simple, universal behavior is true as long as the shift in equilibrium position by the perturbation is small. The relationship between the relaxation time and the rate constants for the reaction is dependent on the rate law. We will consider the example of a temperature jump for a reaction that is second order in the forwards and first order in the reverse direction:

$$A + B \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} C \qquad 3.6.1$$

The effect of the perturbation is to change the equilibrium position from the old value before the temperature change, $[C]_{eq,old}$, to the new equilibrium position at the new temperature after the perturbation, $[C]_{eq}$. The initial value for the relaxation experiment is the old equilibrium concentration, $[C]_o = [C]_{eq,old}$ and the system evolves to the new equilibrium position $[C]_{eq}$, Figure 3.6.3.

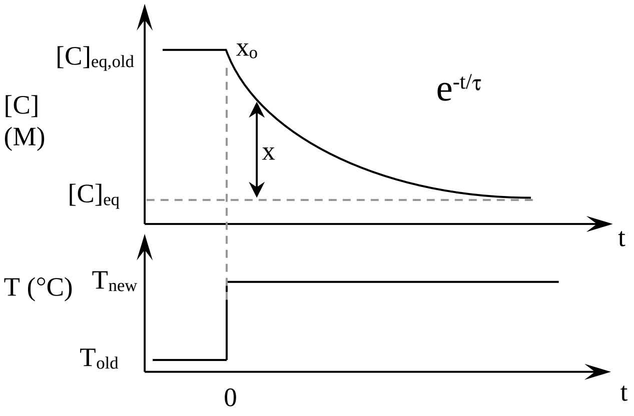


Figure 3.6.3: Temperature jump kinetics is a first-order exponential process with time constant that depends on the rate law. The time of the temperature jump is t = 0.

For the displacement away from equilibrium we define $x \equiv [C] - [C]_{eq}$, where $[C]_{eq}$ is the equilibrium concentration of the product. The displacement is also directly related to the extent of the reaction:

$$x \equiv [C] - [C]_{eq} = ([C]_o + \xi) - ([C]_o + \xi_{eq}) = \xi - \xi_{eq} \qquad 3.6.2$$

Since the stoichiometry is 1:1 the displacement in A is $[A] - [A]_{eq} = -x$. In other words, the $-x$ means that if [C] is less than the equilibrium value then [A] and [B] are greater than the equilibrium value. The stoichiometric relationships are summarized in Table 3.6.1.

Table 3.6.1: Concentrations for an opposed second-order/first-order reaction.

Progress	[A]	[B]	[C]
initial, new T	$[A]_o$	$[B]_o$	$[C]_o$
middle	$[A]_{eq} - x$	$[B]_{eq} - x$	$[C]_{eq} + x$
equilibrium	$[A]_{eq}$	$[B]_{eq}$	$[C]_{eq}$
displacement	$[A] - [A]_{eq} = -x$	$[B] - [B]_{eq} = -x$	$x \equiv [C] - [C]_{eq}$

Assume that the rate law is first order in each reactant and product giving the rate law:

$$\frac{d[C]}{dt} = k_2[A][B] - k_{-1}[C] \qquad 3.6.3$$

To integrate this rate law, it is necessary to express all the concentrations in terms of the displacement, x. At equilibrium, the forward rate is equal to the reverse rate, $k_2[A]_{eq}[B]_{eq} = k_{-1}[C]_{eq}$, or rearranging gives:

$$k_2[A]_{eq}[B]_{eq} - k_{-1}[C]_{eq} = 0 \qquad \text{(equilibrium)} \qquad 3.6.4$$

From Table 3.6.1, $[C] = [C]_{eq} + x$ in the middle of the relaxation process and the rate derivative simplifies to:

$$\frac{d[C]}{dt} = \frac{d([C]_{eq}+x)}{dt} = \frac{dx}{dt} \qquad 3.6.5$$

Substituting the values from Table 3.6.1 and Eq. 3.6.5 into Eq. 3.6.3 gives:

$$\frac{dx}{dt} = k_2([A]_{eq} - x)([B]_{eq} - x) - k_{-1}([C]_{eq}+x) \qquad 3.6.6$$

Multiplying out each term gives:

$$\frac{dx}{dt} = k_2[A]_{eq}[B]_{eq} - k_2[A]_{eq}\, x - k_2[B]_{eq}\, x + k_2x^2 - k_{-1}[C]_{eq} - k_{-1}\, x \qquad 3.6.7$$

Using Eq. 3.6.4, the $k_2[A]_{eq}[B]_{eq}$ and $-k_{-1}[C]_{eq}$ terms cancel. We have now arrived at the critical step. Since the perturbation is small, the displacement away from equilibrium, x, must be small. The term in x^2 should then be negligible. Neglecting the term in x^2 gives:

$$\frac{dx}{dt} = - k_2[A]_{eq}\, x - k_2[B]_{eq}\, x - k_{-1}\, x \qquad 3.6.8$$

Neglecting higher order terms in x guarantees that the relaxation will be a first-order exponential process. Distributing out the common factor of $-x$ gives:

$$\frac{dx}{dt} = - \{k_2([A]_{eq} + [B]_{eq}) + k_{-1}\}\, x \qquad 3.6.9$$

All the terms in the braces are constants. We define the relaxation time:

$$\tau \equiv \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-1}} \qquad (A + B \rightleftarrows C) \qquad 3.6.10$$

Eq. 3.6.9 reduces to:

$$\frac{dx}{dt} = -\frac{x}{\tau} \qquad 3.6.11$$

or equivalently, using Eq.3.6.2:

$$\frac{d(\xi - \xi_{eq})}{dt} = -\frac{(\xi - \xi_{eq})}{\tau} \qquad 3.6.12$$

These last two equations correspond to simple first-order kinetics, which by general pattern ℘***1*** we recognize as a *simple exponential process,* which we integrate to:

$$x = x_o\, e^{-t/\tau} \qquad \text{or} \qquad \xi - \xi_{eq} = (\xi_o - \xi_{eq})\, e^{-t/\tau} \qquad 3.6.13$$

where the initial state immediately after the temperature jump corresponds to $t = 0$, where $x = x_o$, with $x_o = [C]_o - [C]_{eq}$, with $[C]_o = [C]_{eq,old}$. Similarly, in terms of the extent of the reaction, at $t = 0$ the extent is the initial extent, $\xi = \xi_o$, with ξ_o given by the equilibrium position before the temperature jump. The response of the system to the perturbation is a simple first-order relaxation towards the new equilibrium state with time constant τ.

Eq. 3.6.9 only holds for the reaction stoichiometry $A + B \rightleftarrows C$ that is second order forwards and first order backwards. Corresponding equations must be derived for other reaction orders and stoichiometries. We have already done another example. Eq. 3.4.24 corresponds to a first order forwards and first order backwards $A \rightleftarrows B$ reaction. In deriving Eq. 3.4.24 we used the displacement, we just didn't use the symbol x. Comparing Eq. 3.4.24 with Eq. 3.6.13 gives:

$$\tau \equiv \frac{1}{k_1 + k_{-1}} \qquad (A \rightleftarrows B) \qquad 3.6.14$$

Chemical relaxation techniques have greatly extended the types of chemical reactions that can be studied and the range of rate constants that can be determined. An enzyme binding to its substrate to form the enzyme substrate complex, $E + S \rightleftarrows [ES]$, is one important $A + B \rightleftarrows C$ example. We should emphasize the importance of the fact that chemical relaxation, as well as flash photolysis, starts with the system at equilibrium. There is no hurry when mixing the reagents for the reaction. In addition, once the system relaxes back to equilibrium, the perturbation may be repeated. The kinetics determination can be repeated many times with the same reagents. This attribute conserves precious enzymes, nucleic acids, or reagents that are difficult to synthesize.

Example 3.6.1: *Temperature Jump Kinetics*

The equilibrium constant for the reaction $H^+ + OH^- \rightleftarrows H_2O$ is a function of temperature, so the equilibrium position shifts with a temperature jump. The progress of the reaction is followed using conductivity. At 298.2 K at pH 7.000 the relaxation time is 37. μs. Calculate k_2 and k_{-1}. The autoprotolysis constant for water, K_w, is 1.008×10^{-14} and $[H_2O] = 55.33$ M at 298.2 K.

Answer: The rate law for the reaction is:

$$-\frac{d[H^+]}{dt} = k_2\, [H^+][OH^-] - k_{-1}\, [H_2O]$$

At equilibrium for this reaction:

$$K_c = \frac{k_2}{k_{-1}} = \frac{[H_2O]_{eq}}{[H^+]_{eq}[OH^-]_{eq}} = \frac{[H_2O]_{eq}}{K_w} = \frac{55.33}{1.008\text{x}10^{-14}} = 5.489\text{x}10^{15}$$

and at neutral pH, $[H^+]_{eq} = [OH^-]_{eq} = \sqrt{K_w} = 1.004\text{x}10^{-7}$ M. We can also relate the two rate constants through the equilibrium constant by $k_{-1} = k_2/K_c$. From Eq. 3.6.10:

$$\tau = \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-1}} = \frac{1}{k_2([H^+]_{eq} + [OH^-]_{eq}) + k_{-1}}$$

Inverting this last equation and substituting for k_{-1} gives:

$$k_2([H^+]_{eq} + [OH^-]_{eq}) + k_2/K_c = 1/\tau$$

Putting the experimental values in gives:

$$k_2(2.008\text{x}10^{-7}\text{ M}) + k_2(1.822\text{x}10^{-16}) = 2.703\text{x}10^{4}\text{ s}^{-1}$$

Solving for k_2 gives $k_2 = 1.35\text{x}10^{11}\text{ M}^{-1}\text{s}^{-1}$. This rate constant is one of the largest known. Proton transfer rate constants are usually quite large. Finally k_2 and k_{-1} are related through the equilibrium constant, $k_{-1} = k_2/K_c = 2.45\text{x}10^{-5}\text{ s}^{-1}$.

3.7 Summary – Looking Ahead

Rate laws must be determined in the laboratory. To determine the rate law, integrated rate laws are compared to the time course for the reaction assuming different reaction orders. Reaction rates span many orders of magnitude with rate constants from ~$10^{11}\text{ M}^{-1}\text{ s}^{-1}$ to centuries^{-1}. Flash photolysis and chemical relaxation techniques allow the study of fast reactions, starting from equilibrium. The response of any chemical reaction to a small perturbation is an exponential decay that is characterized by a single relaxation time. Once the rate law has been determined, a mechanism can be postulated that predicts the elementary steps that are responsible for the rate law. Mechanisms are the subject of the next chapter. One important question for the next chapter is “why can’t the rate law be determined from the overall reaction stoichiometry?” We also want to focus on systems that involve a complex sequence of reactions.

Chapter Summary

1. A chemical kinetics study has three stages: (1) The determination of the empirical rate law, (2) the determination of the mechanism of the reaction, and (3) the determination of the rate constants for each mechanistic step through first-principles theoretical calculations.
2. The order of the reaction with respect to each constituent is the exponent of the concentration term in the rate law. The overall order is the sum of the orders with respect to each reactant.

3. The mechanism is the sequence of elementary steps that describe the collisions that take place during the course of the reaction. The number of molecules involved in each collision in the mechanism is called the molecularity.
4. The steps in a complete mechanism should add to give the overall reaction.
5. The stoichiometric coefficients are symbolized as ν_i for each of the i constituents. The ν_i are negative for a reactant and positive for a product. The change in the extent of the reaction, $d\xi$, is related to the stoichiometric coefficients:

   $\frac{1}{\nu_i} dn_i = d\xi$ and solving for the change in moles: $dn_i = \nu_i \, d\xi$
6. The rate of the reaction in terms of changes in concentration is given as: $\upsilon = \frac{1}{\nu_i}\frac{dc_i}{dt} = \frac{1}{V}\frac{d\xi}{dt}$
7. The average rate for a reaction during the time interval from t_1 to t_2 is given by:

   $\overline{\upsilon} = \frac{1}{\nu_i}\frac{c_i(t_2) - c_i(t_1)}{t_2 - t_1}$ at $\overline{t} = \frac{t_1 + t_2}{2}$ and $\overline{c} = \frac{c_i(t_1) + c_i(t_2)}{2}$
8. To determine the rate law, there are three general options:
   1. The Integral Method: The time course is compared to the integrated rate laws.
   2. The Half-time Method: The variation of the half-times of the reaction with initial concentration is compared to predictions for different reaction orders.
   3. The Differential Method: The differential method directly follows the average rate of the reaction as a function of the concentrations.
9. The lifetime for a first-order process, τ, is the "1/e time," which is the time necessary for the reactant to drop to 0.368 of its initial concentration. For first-order chemical reactions the 1/e time is equal to 1/k.
10. The lifetime and the half-time of a first-order process are related by $t_{½} = 0.6931\,\tau$.
11. In the Isolation Method the rate law is simplified by setting the concentrations of all the reactants except for one in large excess.
12. Pseudo-order reactions have an effective rate constant that combines the concentration factor of one or more species that are in large excess with the original rate constant. For example, the solvent term is often combined with the rate constant, $k_{eff} = k\,[H_2O]^m$.
13. Any linear concentration measure can be used directly for the determination of the reaction order. For absorbance X = A and for conductivity $X = \kappa$:

   $$\frac{[A]}{[A]_o} = \frac{[A]_o - \xi}{[A]_o} = \frac{X - X_\infty}{X_o - X_\infty} \quad \text{and} \quad \frac{[A]_o - [A]}{[A]_o} = \frac{\xi}{[A]_o} = \frac{X_o - X}{X_o - X_\infty}$$
14. Non-linear curve fitting is the best method for calculating rate constants from the experimental time course.
15. Correlation coefficients between the fit parameters larger than 0.95 usually suggests that one of the fit parameters needs to be specified as a fixed parameter, independently determined either directly from the data or from another experiment.
16. The extent of the reaction in concentration units is ξ/V. Since concentration is intensive, we can assume V = 1 without loss of generality: $[A] = [A]_o - \xi/V$ is equivalent to $[A] = [A]_o - \xi$.

17. For initial rates υ_{o2} and υ_{o1} corresponding to initial concentrations $[A]_{o1}$ and $[A]_{o2}$, the order of the reaction with respect to A, n, is determined from:

$$\ln\left(\frac{\upsilon_{o2}}{\upsilon_{o1}}\right) = n \ln\left(\frac{[A]_{o2}}{[A]_{o1}}\right)$$

18. During the course of the reaction: $\ln \upsilon = n \ln[A] + \ln(k\,[B]^m)$.
19. A reversible reaction from a kinetic standpoint just means the reaction runs forwards and backwards. Thermodynamic reversibility for a chemical reaction requires kinetic reversibility and that the reaction is also at equilibrium.
20. Chemical kinetics describes the irreversible progress of a reaction towards equilibrium.
21. At equilibrium the forward rate is equal to the reverse rate: $k_f\,[A]\,[B] = k_r\,[C]\,[D]$ or $\upsilon_+ = \upsilon_-$
22. The ratio of the forward and reverse rate constants is the equilibrium constant:

$$K_{eq} \equiv \frac{k_f}{k_r} = \left(\frac{[C]\,[D]}{[A]\,[B]}\right)_{eq}$$

23. The displacement of a reaction away from equilibrium for product C is defined as:

$x = [C] - [C]_{eq} = ([C]_o + \xi) - ([C]_o + \xi_{eq}) = \xi - \xi_{eq}$

and for reactant A: $[A] - [A]_{eq} = ([A]_o - \xi) - ([A]_o - \xi_{eq}) = \xi_{eq} - \xi = -x$

24. The Arrhenius equation for the temperature dependence of reaction rate constants is:

$k = A\,e^{-E_a/RT}$ where A is the pre-exponential factor and E_a is the activation energy.

25. The "Chemists Rule:" a typical chemical reaction roughly doubles in rate for every 10 K temperature increase near room temperature. This behavior corresponds to $E_a \approx 50$ kJ mol^{-1} near room temperature.
26. The activation energy is a measure of the collision energy necessary for the bond breaking and making steps in a reaction to occur.
27. The pre-exponential factor is the product of the rate of intermolecular collisions and a probability factor that depends on the collision geometry and the timing of the collision.
28. In solution, the solvent can act as a cage surrounding both reactants so that many collisions occur when the reactants approach each other at short range. These constrained multiple collisions are called molecular encounters.
29. The temperature dependence is sometimes better expressed as: $k = a\,T^m\,e^{-E_a/RT}$
30. Stopped flow instruments automate the rapid mixing of the reactants.
31. Flash photolysis instruments use short light pulses to initiate photochemical reactions.
32. Chemical relaxation techniques use a sudden perturbation in temperature, pressure, electric field, or concentration to shift the position of equilibrium for a reacting system. After the perturbation, the system is monitored as a function of time as the system approaches the new equilibrium position.
33. The response of a chemical reaction to a perturbation is simple first-order relaxation towards the new equilibrium state with time constant τ: $x = x_o\,e^{-t/\tau}$ or $\xi - \xi_{eq} = (\xi_o - \xi_{eq})\,e^{-t/\tau}$
34. For first order forwards and first order reverse with stoichiometry $A \rightleftarrows B$: $\tau \equiv \dfrac{1}{k_1 + k_{-1}}$
35. For second order forwards and first order reverse with stoichiometry $A + B \rightleftarrows C$:

$$\tau \equiv \frac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-1}}$$

Summary Table: Integrated Rate Laws (including formulas from the Problems)

Stoichiometry	Rate Law	Integrated Form	Linear Form
zeroth order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_o$	$[A] = [A]_o - k_o\,t$	$[A] - [A]_o = -k_o\,t$
½ order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_{1/2}\,[A]^{1/2}$	$[A] = \left([A]_o^{1/2} - \frac{k_{1/2}}{2}\,t\right)^2$	$[A]^{1/2} - [A]_o^{1/2} = -\frac{k_{1/2}}{2}\,t$
¾ order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_{3/4}\,[A]^{3/4}$	$[A] = \left([A]_o^{1/4} - \frac{k_{3/4}}{4}\,t\right)^4$	$[A]^{1/4} - [A]_o^{1/4} = -\frac{k_{3/4}}{4}\,t$
1st order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_1\,[A]$	$[A] = [A]_o\,e^{-k_1 t}$	$\ln\left(\frac{[A]}{[A]_o}\right) = -k_1 t$
1st order $2\,A \rightarrow P$	$-\frac{d[A]}{dt} = 2\,k_1\,[A]$	$[A] = [A]_o\,e^{-2k_1 t}$	$\ln\left(\frac{[A]}{[A]_o}\right) = -2k_1 t$
1st order $A \rightleftarrows B$	$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$	$[A] = ([A]_o - [A]_{eq})e^{-(k_1 + k_{-1})t} + [A]_{eq}$	$\ln\left(\frac{[A]-[A]_{eq}}{[A]_o-[A]_{eq}}\right) = -(k_1 + k_{-1})\,t$
2nd order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_2\,[A]^2$	$[A] = \frac{1}{\frac{1}{[A]_o} + k_2\,t}$	$\frac{1}{[A]} - \frac{1}{[A]_o} = k_2\,t$
2nd order $2\,A \rightarrow P$	$-\frac{d[A]}{dt} = 2k_2\,[A]^2$	$[A] = \frac{1}{\frac{1}{[A]_o} + 2k_2\,t}$	$\frac{1}{[A]} - \frac{1}{[A]_o} = 2k_2\,t$
2nd order $A \rightarrow P$	$\frac{d\xi}{dt} = k_2\,([A]_o - \xi)^2$	$\xi = [A]_o - \frac{1}{\left(\frac{1}{[A]_o} + k_2\,t\right)}$	$\frac{1}{[A]_o - \xi} - \frac{1}{[A]_o} = k_2\,t$
2nd order $A + B \rightarrow P$	$\frac{d\xi}{dt} = k_2\,([A]_o - \xi)([B]_o - \xi)$	$\xi = \frac{[B]_o\left(1 - e^{([B]_o - [A]_o)k_2 t}\right)}{\left(1 - \frac{[B]_o}{[A]_o}e^{([B]_o - [A]_o)k_2 t}\right)}$	$\frac{1}{[B]_o - [A]_o}\ln\left(\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - \xi)}\right) = k_2 t$
3rd order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_3\,[A]^3$	$[A] = \frac{1}{\left(\frac{1}{[A]_o^2} + 2k_3 t\right)^{1/2}}$	$\frac{1}{2[A]^2} - \frac{1}{2[A]_o^2} = k_3 t$
3rd order $2A + B \rightarrow P$	$\frac{d\xi}{dt} = k_3([A]_o - 2\xi)^2([B]_o - \xi)$	$\frac{1}{2[B]_o - [A]_o}\left[\frac{2\xi}{[A]_o([A]_o - 2\xi)} - \frac{1}{2[B]_o - [A]_o}\ln\left(\frac{[A]_o([B]_o - \xi)}{[B]_o([A]_o - 2\xi)}\right)\right] = k_3 t$	

℘4 Exponential Temperature Dependence: $e^{-E/RT}$: The Arrhenius equation and similar equations of the general type $e^{-E/RT}$ can be alternatively expressed in the forms:

$$k = A\,e^{-E/RT} \qquad \ln k = \ln A - \frac{E}{RT} \qquad \ln\frac{k_{T2}}{k_{T1}} = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad k_{T2} = k_{T1}\,e^{-\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

The temperature dependence can be expressed in terms of $\Delta T = T_2 - T_1$:

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\left(\frac{T_2 - T_1}{T_1\,T_2}\right) = -\left(\frac{\Delta T}{T_1\,T_2}\right) \cong -\left(\frac{\Delta T}{T_1^2}\right)$$

The last approximation only holds for narrow temperature ranges.

The “Chemists Rule” is a rough approximation given by:

$$k_{T2} \approx k_{T1}\ e^{\left(\frac{E_a}{RT_1^2}\right)\Delta T}$$

which only holds for narrow temperature ranges. Similar approximate doubling rules can be expressed for other examples of $e^{-E/RT}$ temperature dependence.

Summary Table: Reaction Half-times (including formulas from the Problems)

Stoichiometry	Rate Law	Half-time
zeroth order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_o$	$t_{½} = \frac{[A]_o}{2k_o}$
zeroth order $2\ A \rightarrow P$	$-\frac{d[A]}{dt} = 2\ k_o$	$t_{½} = \frac{[A]_o}{4k_o}$
½ order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_{½}\ [A]^{½}$	$t_{½} = \frac{0.586\ [A]_o^{½}}{k_{½}}$
¾ order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_{¾}\ [A]^{¾}$	$t_{½} = \frac{0.636\ [A]_o^{¼}}{k_{¾}}$
1st order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_1\ [A]$	$t_{½} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$
1st order $2\ A \rightarrow P$	$-\frac{d[A]}{dt} = 2\ k_1\ [A]$	$t_{½} = \frac{\ln 2}{2k_1} = \frac{0.693}{2k_1}$
1st order $A \rightleftarrows B$	$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$	$t_{½} = \frac{\ln 2}{(k_1 + k_{-1})} = \frac{0.693}{(k_1 + k_{-1})}$
2nd order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_2\ [A]^2$	$t_{½} = \frac{1}{[A]_o k_2}$
2nd order $2\ A \rightarrow P$	$-\frac{d[A]}{dt} = 2k_2\ [A]^2$	$t_{½} = \frac{1}{2[A]_o k_2}$
3rd order $A \rightarrow P$	$-\frac{d[A]}{dt} = k_3\ [A]^3$	$t_{½} = \frac{3}{2[A]_o^2\ k_3}$

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Problems: Kinetics

1. In Example 3.3.1 we discussed denitrification of contaminated ground water. The literature assumes a half-order reaction with respect to NO_3^-, but the differential method for the particular data set gives ¾ order. The best fit values for the corresponding rate constants are $k_{1/2} = 26.71$ and $k_{3/4} = 7.12$. Give the units for the rate constants with the concentration expressed in mg L^{-1}.

2. The half-life of the pesticide aldicarb (trade name Temik) is 30.0 days. The decomposition of aldicarb is first-order. Calculate the time necessary for the amount of adicarb in a soil sample to drop to 10.0% of its initial value.

3. Organisms require iron for survival. Reduced iron in the form of Fe^{2+} is readily available for acquisition by living systems. However, Fe^{2+} is oxidized by O_2 from the air to produce Fe^{3+}, which precipitates from solution as mixed hydrated oxides and hydroxides. Iron(II) stability is strongly pH dependent. The oxidation of Fe^{2+} in aqueous 0.5 M $HClO_4$ solution at 35°C follows the rate law:

$$-\frac{d[Fe^{2+}]}{dt} = k\,[Fe^{2+}]^2\, P_{O_2}$$

where P_{O_2} is the partial pressure of O_2 above the solution and $k = 3.65\text{x}10^{-3}$ mol^{-1} L atm^{-1} hr^{-1}. Assume that the air above the solution is at constant $P_{O_2} = 0.200$ atm. (a) Calculate the half-time of the reaction in days for an initial concentration of 0.100 M Fe^{2+}. (b). How long would it take for the concentration of Fe^{2+} to drop to 0.0100 M?

4. The concentration of ozone, O_3, in the stratosphere is dependent on interactions with the odd electron reactive nitrogen species, NO. The concentration of NO in the atmosphere is determined in part by the rate of oxidation by O_2:

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2$$

An initial rate study at 25°C was completed with the following results. Determine the rate law and the rate constant. The initial rate is the slope of the time course for very short times, $t \approx 0$:

$$\text{initial rate} = \upsilon_o = -\left(\frac{d[O_2]}{dt}\right)_o$$

Exp	$[O_2]_o$ (mol L^{-1})	$[NO]_o$ (mol L^{-1})	υ_o (mol $L^{-1}\ s^{-1}$)
1	$1.44\text{x}10^{-3}$	$0.28\ \text{x}10^{-3}$	$6.90\text{x}10^{-7}$
2	$1.44\ \text{x}10^{-3}$	$0.93\ \text{x}10^{-3}$	$7.50\ \text{x}10^{-6}$
3	$1.44\ \text{x}10^{-3}$	$2.69\ \text{x}10^{-3}$	$6.00\ \text{x}10^{-5}$
4	$6.60\ \text{x}10^{-5}$	$2.69\ \text{x}10^{-3}$	$3.00\ \text{x}10^{-6}$

5. The decomposition of acetaldehyde:

$$CH_3CH{=}O \rightarrow CH_4 + C{\equiv}O$$

at 518°C and at an initial pressure of 363 mm Hg can be monitored by measuring the total pressure of the reaction at constant volume.[1] What is the order of the reaction and the rate constant? Use non-linear curve fitting. [Hint: you need to solve for the partial pressure of acetaldehyde from the total pressure.]

t (s)	42	73	105	190	242	310
P (mm Hg)	397	417	437	477	497	517
t (s)	384	480	665	840	1070	1440
P (mm Hg)	537	557	587	607	627	647

6. Redo the kinetic analysis for the data from Problem 5 using the linearized forms of the integrated rate laws.

7. Use the differential method during the time course for the data in Problem 5.

8. Pharmacokinetics is the study of the absorption, disposition, metabolism, and excretion (ADME) of drugs in living organisms. Pharmacokinetics uses chemical kinetics as a tool to predict drug levels in the body and anticipate drug distribution problems that might arise. Your study of chemical kinetics puts you in a good position to understand ADME properties of drug substances. In the terminology of pharmacology, a bolus dose is a drug given in a short period of time, for example by intravenous injection or oral tablet administration. The table, below, gives the plasma concentration as a function of time after the administration of a 184-mg bolus dose of ceftriaxone to a newborn infant.[2,3] Ceftriaxone is an antibiotic. Find the effective kinetic order for the time course of the drug concentration, the rate constant, and half-life of the drug in the body.

t (hr)	1.0	6.0	12.	24.	48.	72.	96.	144.
Concentration (mg L^{-1})	137.	120.	103.	76.	42.	23.	12.	3.7

9. The absorption of UV light by benzophenone creates a long-lived excited state. When isopropanol-water mixtures are used as the solvent, the excited state of benzophenone rapidly reacts with isopropanol to produce protonated benzophenone ketyl $(C_6H_5)_2CO^{\bullet}H$, which is a free radical:

$$(C_6H_5)_2CO^* + (CH_3)_2CHOH \rightarrow (C_6H_5)_2CO^{\bullet}H + (CH_3)_2C^{\bullet}OH$$

The “*” indicates an electronic excited state. In basic solution protonated benzophenone ketyl rapidly looses a proton to produce the benzophenone ketyl radical anion:

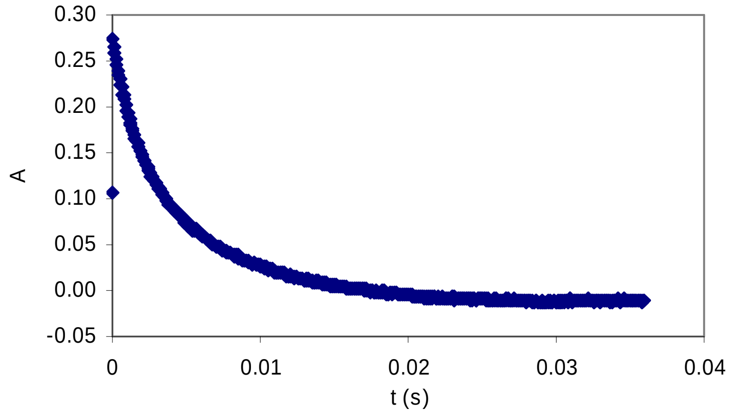
$$(C_6H_5)_2CO^{\bullet}H \rightleftarrows (C_6H_5)_2CO^{\bullet-} + H^+$$

The benzophenone ketyl radical anion then reacts with the protonated form to produce benzpinacol:

$$(C_6H_5)_2CO^{\bullet}H + (C_6H_5)_2CO^{\bullet-} \xrightarrow{k_2} (C_6H_5)_2C(OH)\text{-}C(OH)(C_6H_5)_2$$

The benzophenone ketyl radical anion has an absorption maximum at 630 nm, which allows the disappearance of the radical anion to be followed as a function of time in a laser flash photolysis instrument. The absorbance time course for the reaction is given below. The data table is extracted from the much larger data file from the instrument, which is plotted at right. Find the order of the reaction and the rate constant with respect to benzophenone ketyl radical anion using non-linear least squares curve fitting.

t (ms)	A
0.064	0.2736
0.128	0.2660
3.264	0.1080
6.464	0.0540
9.664	0.0282
12.864	0.0129
16.064	0.0029
19.264	-0.0039
22.464	-0.0084
25.664	-0.0109
28.864	-0.0125
32.064	-0.0111
35.264	-0.0102



10. Use the data in the last problem with linear curve fitting to determine the order of the reaction and the rate constant.

11. Determine the fluorescence lifetime for anthracene using the following fluorescence intensity measurements.

t (ns)	0	2	4	6	8	10
Intensity	62620	41250	27218	17708	11352	7560

12. Determine the integrated rate law for a zeroth-order reaction with stoichiometry 2 A → P. Use definite integrals. Zeroth-order reactions are common with reactions involving surfaces. Find the half-time for a zeroth-order reaction with this stoichiometry.

13. The half-time for a chemical reaction is the time when ½ the original amount of reactant remains. However, the choice of the half-time point as a measure of the reaction rate is not unique. We can also determine the time when ¼ of the original amount remains, or when 1/p of the original amount remains. Find the formula that relates the time to reach the 1/p point to the rate constant, for a first-order and a second-order reaction.

14. Determine the integrated rate law and the half-time for a third-order reaction with the stoichiometry A → P.

15. Determine the integrated rate law for a half-order reaction with the stoichiometry A → P.

16. In biology, exponential population growth arises from the rate law:

$$\frac{d[P]}{dt} = k\,[P]$$

where [P] is the population of a given organism and d[P]/dt is the birth rate. In short, the greater the number of individuals the greater the birth rate. Find the integrated rate law for the population.

17. Determine the integrated rate law for a ¾-order reaction with the stoichiometry A → P.

18. In Example 3.3.1 we discussed denitrification of contaminated ground water. The literature assumes a ½-order reaction with respect to NO_3^-, but the differential method for the data set gives ¾ order. Plot the time course for a ½-order and a ¾-order reaction using $[NO_3^-]_o = 409\ \text{mg L}^{-1}$ for 0 hr to 1.7 hr. Include the data points from Example 3.3.1. The best fit values for the rate constants are $k_{½} = 26.71\ \text{mg}^{-½}\ \text{L}^{½}\ \text{hr}^{-1}$ and $k_{¾} = 7.12\ \text{mg}^{-¾}\ \text{L}^{¾}\ \text{hr}^{-1}$. [Hint: restrict the time interval for the half-order plot so that $([A]_o^{½} - k_{½}\, t/2) \geq 0$ or for the ¾-order plot, $([A]_o^{¼} - k_{¾}\, t/4) \geq 0$]

19. Find the integrated rate law for a third-order reaction that is second-order in A and first-order in B for the stoichiometry: 2 A + B → products. In actual examples, B is often called a "third body" and is often an inert gas, an N_2 molecule from the air, a particle, or the walls of the container. If the third body were not present, the collision of two A molecules would not be stable and would dissociate back to form two A molecules. The third body is necessary to carry away the excess energy of the collision. [Grab your integral tables for this one.]

20. The *cis-trans* isomeration of 1-ethyl-2-methylcyclopropane is first order in the forward and reverse directions:[4,5]

$$\textit{cis} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \textit{trans}$$

The reaction, starting with only *cis* isomer has the following time course. The long-time value for the *cis*-isomer concentration is 0.00443 M. Determine k_1 and k_{-1}.

t (s)	0	400	1000	1600	2100
[*cis*] (M)	0.01679	0.01406	0.01102	0.00892	0.00775

21. The rate of decomposition of acetaldehyde has been studied as a function of temperature. The table below gives the rate constant for the reaction as a function of temperature. Determine the activation energy and the pre-exponential factor.

T (K)	703	733	759	791	811	836
k_2 (M^{-1} s^{-1})	0.011	0.035	0.105	0.343	0.79	2.14

22. This problem concerns the error analysis of the results from the last problem. (a) Using the results from the last problem, determine the error in the activation energy and the pre-exponential factor. (b) Often a better approach is to use a non-linear fit. Do a non-linear fit to the original data in the last problem and compare the fit values and the uncertainties with the linearized fit.

23. Calculate the activation energy and pre-exponential factor for the decomposition of N_2O_5 from the following temperature dependence.[6]

T (K)	298.0	308.0	318.0	328.0	338.0
k_1 (min^{-1})	2.03	8.09	29.9	90.1	291.5

24. The rate constant for the disappearance of chlorine in the reaction of NO with Cl_2 to form NOCl is 4.52 M^{-2} s^{-1} at 0.0°C and 8.03 M^{-2} s^{-1} at 22.0°C. What are the activation energy and pre-exponential factor for this reaction?

25. The decomposition of urea is $NH_2CONH_2 + 2\ H_2O \rightarrow 2\ NH_4^+ + CO_3^-$. The activation energy for the reaction is 128.0 kJ mol^{-1}. The rate constant 71.2°C is $2.77\text{x}10^{-5}$ min^{-1}. Calculate the rate constants at 40.0°C.

26. The rate constant for the decomposition of N_2O_5 is 8.09 min^{-1} at 308.0 K and 90.1 min^{-1} at 328.0 K.[6] Calculate the rate constant at 298.2 K.

27. The half-time for the first-order denaturation of yeast invertase at 55.0°C and pH 3 is 26.7 min. The activation energy is 308. kJ mol^{-1}.[7] Calculate the time for the denaturation of the protein to be 75% complete at 60.0°C.

28. The development of biological complexity and the emergence of life have important time constraints. These time constraints in turn give a corresponding range of reaction rate constants for the production of the building blocks of life. All reactions are reversible, and the ratio of the forward and reverse rate constants is given by the equilibrium constant, $K_{eq} = k_f/k_r$. Favorable equilibrium is required to allow the significant build-up of products. A careful balancing of rate and equilibrium constants is necessary for the persistence necessary to build molecular and organizational complexity. If reactions are two fast, complexity can’t be established because the lifetimes of the molecules are too short. If reactions are too slow, interdependent sets of complex reaction sequences can’t develop. The range of reaction half-times that are amenable for the building of complexity is estimated to be in the 1 s to 100 yr range, which still spans more than 9

orders of magnitude.[8] Assume a range of pseudo-first order half-times of 1 s to 100 yr to calculate the range of amenable activation energies for reactions to build complexity at 298 K. Typical pre-exponential factors are in the range of $1.0\text{x}10^{10}\ \text{s}^{-1}$ to $1.0\text{x}10^{11}\ \text{s}^{-1}$.

29. In this problem we compare the integrated rate law for $A + B \rightarrow P$ with $A \rightarrow P$ for a simple first-order and second-order reaction. (a) For a second-order reaction that is first order in A and first order in B, solve Eq. 3.2.52 for ξ. Then plot $[A] = [A]_o - \xi$ using the initial conditions $[A]_o = 0.5$ M, $[B]_o = 1.0$ M and $k_2 = 0.1\ \text{M}^{-1}\ \text{s}^{-1}$. Let t range from 0 to 20 s. (b) On the same axis, plot the corresponding time course for a first-order reaction, $A \rightarrow P$, with $[A]_o = 0.5$ M and $k_1 = 0.1\ \text{s}^{-1}$. (c) On the same axis, plot the corresponding time course for a simple second-order reaction of the form and stoichiometry $A \rightarrow P$. For this last plot, use a rate constant of $k_2 = 0.2\ \text{M}^{-1}\ \text{s}^{-1}$ so that the initial rates for all three types of reactions are equal, to make a fair comparison. (d) Rationalize the differences in the plots.

30. Show that Eq. 3.4.22 reduces to simple first-order behavior, with a rate constant of just k_1, for a reaction that runs to completion.

31. Find the lifetime and half-time for a reversible first-order/first-order reaction from Eq. 3.4.23:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

32. For a reversible first-order/first-order reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

(a) Show that the displacement for A after n half-times is given by:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{2}\right)^n$$

(b)What percentage of the initial displacement for A remains after five half-times?

33. For a reversible first-order/first-order reaction:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$$

(a) Show that the displacement for A after n lifetimes is given by:

$$[A] - [A]_{eq} = ([A]_o - [A]_{eq}) \left(\frac{1}{e}\right)^n$$

A commonly quoted rule is that a reaction or process has essentially returned to equilibrium after five lifetimes. (b)What percentage of the initial displacement for A remains after five lifetimes?

34. Show that the relaxation time for a dimerization is $\tau = \dfrac{1}{(4k_2[A]_{eq} + k_{-1})}$ with:

$$2\,A \; \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} \; A_2$$

Assume the reaction is second-order in the forward and first-order in the reverse direction.

35. Consider the reaction: $A + B \rightleftarrows C + D$
Show that the displacement for each product is x and for each reactant is – x, independent of the initial concentrations used to prepare the reaction mixture.

36. Consider a temperature jump perturbation for a reaction that is second order in the forwards and second order in the reverse direction:

$$A + B \; \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \; C + D$$

Show the relaxation time is: $\tau \equiv \dfrac{1}{k_2([A]_{eq} + [B]_{eq}) + k_{-2}([C]_{eq} + [D]_{eq})}$

37. Consider a temperature jump perturbation for a reaction that is second order in the forwards and second order in the reverse direction and catalyzed by C:[9]

$$A + C \; \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \; B + C$$

Given the catalyst concentration is $[C]_o$, show that the relaxation time is: $\tau = \dfrac{1}{(k_2 + k_{-2})[C]_o}$

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