LECTURE 2

Reaction Kinetics

LECTURE OVERVIEW: I present some methods for characterizing reactions in natural waters. Then several graphical and computer methods are outlined to determine the order and rate of a reaction. In addition I review the reaction stoichiometry and the effect of temperature.

As described in Fig. 1.5, a number of things can happen to a pollutant once it enters a water body. Some of these relate to transport. For example it can be translated and dispersed by currents within the system. In addition the pollutant can exit the system by volatilization, by sedimentation, or by transport along with outflowing water. All these mechanisms affect the pollutant without altering its chemical composition. In contrast the pollutant might be transformed into other compounds via chemical and biochemical reactions. In this lecture we focus on such reactions.

Suppose that you want to perform an experiment to determine how a pollutant reacts after it enters a natural water. A simple approach would be to introduce some of the pollutant into a series of bottles filled with the water. A stirrer could be included in each bottle to keep the contents well mixed. Such vessels are commonly referred to as ***batch reactors***. By measuring concentration in each bottle over time, you would develop data for time and concentration (Fig. 2.1).

The purpose of this lecture is to explore how such data can be employed to characterize the reactions that affect the pollutant. That is, we will investigate how to quantitatively summarize (model) the reaction.

2.1 REACTION FUNDAMENTALS

Before discussing how reactions can be quantified, we must first develop some general definitions and nomenclature.

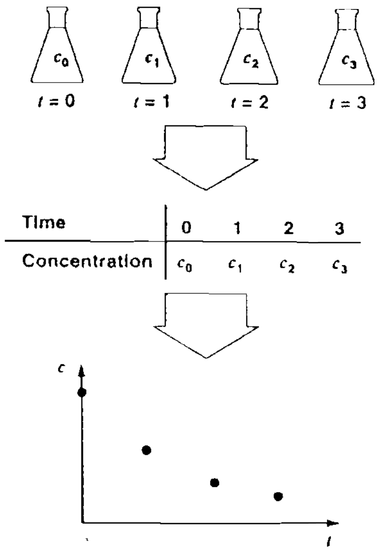


FIGURE 2.1
A simple experiment to collect rate for a pollutant in a natural water.

2.1.1 Reaction Types

Heterogeneous reactions involve more than one phase, with the reaction usually occurring at the surfaces between phases. In contrast a ***homogeneous reaction*** involves a single phase (that is, liquid, gas, or solid). Because they are the most fundamental type of reaction employed in water-quality modeling, this lecture focuses on homogeneous reactions that take place in the liquid phase.

A ***reversible reaction*** can proceed in either direction, depending on the relative concentrations of the reactants and the products:

$$aA + bB \rightleftharpoons cC + dD \tag{2.1}$$

where the lowercase letters represent stoichiometric coefficients and the uppercase letters designate the reacting compounds. Such reactions tend to approach an equilibrium state where the forward and backward reactions are in balance. They are the basis for the area known as ***equilibrium chemistry***. We will return to these types of reactions when we address the topic of pH later in the book.

Although reversible reactions are important in water-quality modeling, more emphasis has been placed on ***irreversible reactions***. These proceed in a single direction and continue until the reactants are exhausted. For these cases, we are dealing with the determination of the rate of disappearance of one or more of the substances that is taking part in the reaction. For example for the irreversible reaction

$$aA + bB \rightarrow cC + dD \tag{2.2}$$

we might be interested in determining the rate at which substance A disappears.

A common example of an irreversible reaction is the decomposition of organic matter, which can be represented generally by where $C_6H_{12}O_6$ is glucose, which can be taken as a simple representation of organic matter. When sewage is discharged into a receiving water, a reaction of this type takes place. The organic matter in the sewage is oxidized by bacteria to form carbon dioxide and water. Although photosynthesis (that is, plant growth) represents a reverse reaction that produces organic matter and oxygen, it does not usually occur in the same vicinity as the decomposition. In addition because decomposition and photosynthesis are relatively slow, they would not come to equilibrium on the time scales of interest in most water-quality problems. Therefore the decomposition is usually characterized as a one-way process.

2.1.2 Reaction Kinetics

The kinetics or rate of such reactions can be expressed quantitatively by the ***law of mass action,*** which states that the rate is proportional to the concentration of the reactants. This rate can be represented generally as

$$\frac{dc_A}{dt} = -kf(c_A, c_B, \ldots) \tag{2.4}$$

This relationship is called a ***rate law.*** It specifies that the rate of reaction is dependent on the product of a temperature-dependent constant k and a function of the concentrations of the reactants f $(c_A, c_B, \ldots)$.

The functional relationship f $(c_A, c_B, \ldots)$ is almost always determined experimentally. A common general form is

$$\frac{dc_A}{dt} = -kc_A^{\alpha}c_B^{\beta} \tag{2.5}$$

The powers to which the concentrations are raised are referred to as the ***reaction order.*** In Eq. 2.5 the reaction is α order with respect to reactant A and β order with respect to reactant B. The overall order of the reaction is

$$n = \alpha + \beta \tag{2.6}$$

The overall order of the reaction, or the order with respect to any individual component, does not have to be an integer. However, several of the most important reactions used in water-quality modeling exhibit integer orders.

In this lecture we focus on a single reactant. For this case Eq. 2.5 is often simplified as

$$\frac{dc}{dt} = -kc^n \tag{2.7}$$

where c = the concentration of the single reactant and n = the order.

2.1.3 Zero-, First-, and Second-Order Reactions

Although there are an infinite number of ways to characterize reactions, Eq. 2.7 with

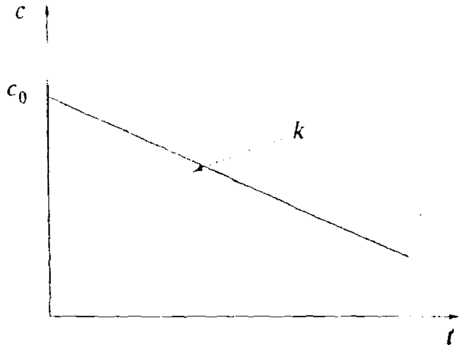


FIGURE 2.2
Plot of concentration versus time for a zero-order reaction

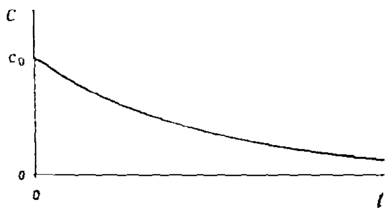


FIGURE 2.3
Plot of concentration versus time for a first-order reaction.

Zero-order. For the zero-order model (n = 0), the equation to integrate is

$$\frac{dc}{dt} = -k \tag{2.8}$$

where k has units of M L^{-3} T^{-1}. If $c = c_0$ at t = 0, then this equation can be integrated by separation of variables to yield

$$c = c_0 - kt \tag{2.9}$$

As denoted by this equation and the graph in Fig. 2.2, this model specifies a constant rate of depletion per unit time. Thus, if a plot of concentration versus time yields a straight line, we can infer that the reaction is zero-order.

First-order. For the first-order model the equation to integrate is

$$\frac{dc}{dt} = -kc$$

where k has units of T^{-1} (see Box 2.1). If $c = c_0$ at t = 0, then this equation can be integrated by separation of variables to yield

$$\ln c - \ln c_0 = -kt \tag{2.11}$$

Taking the exponential of both sides gives

$$c = c_0e^{-kt} \tag{2.12}$$

As denoted by this equation, this model specifies an exponential depletion; that is, the concentration halves per unit time. Thus, as in Fig. 2.3, the concentration curve asymptotically approaches zero with time.

BOX 2.1. The "Meaning" of a First-Order Rate Constant

You may have noticed that the units of the reaction rate depend on the order of the restates that a zero-order decay reaction has a rate of 0.2 mg L^{-1} d^{-1}, it simply means that the substance is disappearing at a rate of 0.2 mg L^{-1} every day.

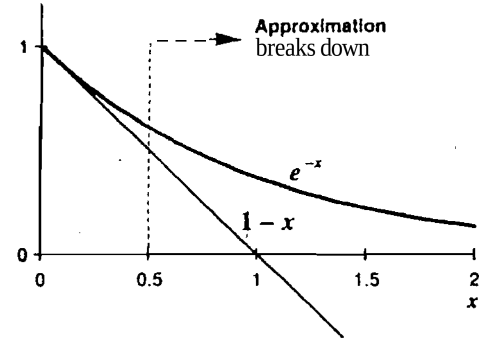
In contrast a first-order rate of 0.1 yr^{-1} is not as straightforward. What does it "mean?" A way to gain insight is provided by the Maclaurin series approximation of the exponential function:

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + $$

If the series is truncated after the first-order term, it is

$$e^{-x} \cong 1 - x$$

As depicted in Fig. B2.1, we see that the first-order approximation describes the rate of decrease well for small values of x. Below $x = 0.5$ the discrepancy is less than 20%. At higher values the approximation and the true value diverge.



TMDL

FIGURE B2.1
Plot of the exponential function along with the first-order **Maclaurin**-series approximation.

This leads us to the following interpretation of the "meaning" of the first-order rate constant. If its magnitude is less than 0.5, it can loosely be interpreted as the fraction of the pollutant that is lost per unit time. Thus a rate of 0.1 yr^{-1} means that 0.1 or 10% is lost in a year. If the magnitude of the rate is higher than 0.5, a change of the units can be used to interpret it. For example a rate of 6 d^{-1} clearly cannot be interpreted as meaning that 600% goes away per day. However, by converting it to an hourly rate,

$$k = 6\ d^{-1}\left(\frac{1\ d}{24\ hr}\right) = 0.25\ hr^{-1}$$

we can state that 25% goes away per hour.

The decay rate used in Eq. 2.12 is called a "base-e" rate, because it is used in conjunction with the exponential function to define the depletion of concentration with time. It should be noted that any base can be employed to describe the same trend. For example it should be recognized that the base-e or Naperian logarithm is related to the base-10 or common logarithm by

$$\ln x \qquad \ln x$$

This relationship can be substituted into Eq. 2.11 to give

$$\log c - \log c_0 = -k't \tag{2.14'}$$

where k' = a "base-10" rate that is related to the base-e rate by

$$k' = \frac{k}{2.3025} \tag{2.15}$$

Taking the inverse logarithm of Eq. 2.14 yields

$$c = c_0 10^{-k't} \tag{2.16}$$

This equation yields identical predictions to Eq. 2.12.

Although most first-order rates are written in terms of base-e, some are expressed in base-10. Therefore it is important to understand which base is being used. Misinterpretation would lead to using a rate that was incorrect by a factor of 2.3025 (Eq. 2.15).

Second-order. For the second-order model the equation to evaluate is

$$\frac{dc}{dt} = -kc^2 \tag{2.17}$$

where k has units of $L^3\ M^{-1}\ T^{-1}$. If $c = c_0$ at $t = 0$, then this equation can be integrated by separation of variables to yield

$$\frac{1}{c} = \frac{1}{c_0} + kt \tag{2.18}$$

Therefore if the reaction is second-order, a plot of $1/c$ versus t should yield a straight line. Equation 2.18 can also be expressed in terms of concentration as a function of time by inverting it to give

$$c = c_0 \frac{1}{1 + kc_0 t} \tag{2.19}$$

Thus, as was the case for the first-order reaction, the concentration approaches zero in a curved, asymptotic fashion.

Finally it should be obvious that a pattern is emerging that can be employed to model higher order rates. That is, for positive integer values of n, where $n \neq 1$,

$$\frac{1}{c^{n-1}} = \frac{1}{c_0^{n-1}} + (n-1)kt \tag{2.20}$$

or solving for c,

$$c = c_0 \frac{1}{\left[1 + (n-1)kc_0^{n-1}t\right]^{1/(n-1)}} \tag{2.21}$$

۲۸

2.2 ANALYSIS OF RATE DATA

There are a variety of ways to analyze batch-reactor data of the type 'shown in use Eq. 2.7 as the basis for illustrating these techniques, many of the general ideas apply to other rate models.

2.2.1 The Integral Method

The integral method consists of guessing n and integrating Eq. 2.7 to obtain a function, $c(t)$. Graphical methods are then employed to determine whether the model fits the data adequately.

The graphical approaches are based on linearized versions of the underlying models. For the zero-order reaction, merely plotting c versus t should yield a straight line (Eq. 2.9). For the first-order reaction, Eq. 2.11 suggests a semi-log plot. These and the other commonly applied models are summarized in Table 2.1.

TMDL

TABLE 2.1
Summary of the plotting strategy used for applying the integral method to irreversible, unimolecular reactions

Order	Rate units	Dependent (y)	Independent (x)	Intercept	Slope
Zero ($n = 0$)	$M(L^3 T)^{-1}$	c	I	c_0	$-k$
First ($n = 1$)	T^{-1}	$\ln c$	I	$\ln c_0$	$-k$
Second ($n = 2$)	$L^3(M T)^{-1}$	$1/c$	I	$1/c_0$	k
General (n # 1)	$(L^3 M^{-1})^{n-1}T^{-1}$	c^{1-n}	I	c_0^{1-n}	$(n - 1)$k

EXAMPLE 2.1. INTEGRAL METHOD. Employ the integral method to determine whether the following data is zero-, first-, or second-order:

t (d)	0	1	3	5	10	15	20
c (mg L^{-1})	12	10.7	9	7.1	4.6	2.5	1.8

If any of these models seem to hold, evaluate k and c_0.

Solution; Figure 2.4 shows plots to evaluate the order of the reaction. Each includes the data along with a best-fit line developed with linear regression. Clearly the plot of In c versus I most closely approximates a straight line. The best-fit line for this case is

$$\ln c = 2.47 - 0.09721 \qquad (r^2 = 0.995)$$

Therefore the estimates of the two model parameters are

$$k = 0.0972\,d^{-1}$$
$$c_0 = e^{2.47} = 11.8 \text{ mg } L^{-1}$$

Thus the resulting model is

$$c = 11.8e^{-0.0972t}$$

The model could also be expressed to the base 10 by using Eq. 2.15 to calculate

0 0972

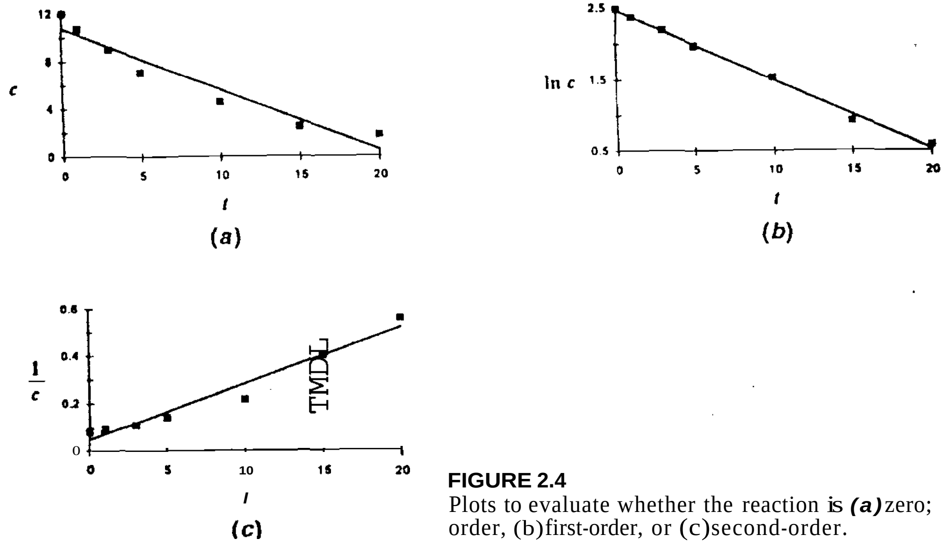


FIGURE 2.4
Plots to evaluate whether the reaction is (a) zero-order, (b) first-order, or (c) second-order.

which can be substituted into Eq. 2.16,

$$c = 11.8(10)^{-0.0422t}$$

The equivalence of the two expressions can be illustrated by computing c at the same value of time,

$$c = 11.8e^{-0.0972(5)} = 7.26$$
$$c = 11.8(10)^{-0.0422(5)} = 7\ 26$$

Thus they yield the same result

2.2.2 The Differential Method

The differential method applies a logarithmic transform to Eq. 2.7 to give

$$\log\left(-\frac{dc}{dt}\right) = \log k + n \log c \tag{2.22}$$

Therefore if the general model (Eq. 2.7) holds, a plot of the log(– dcldt) versus log c should yield a straight line with a slope of n and an intercept of log k.

The differential approach has the advantage that it automatically provides an estimate of the order. It has the disadvantage that it hinges on obtaining a numerical estimate of the derivative. This can be done in several ways. One of the most common is based on numerical differentiation.

Numerical differentiation. Numerical differentiation uses finite-difference approximations to estimate derivatives (Chapra and Canale 1988). For example a

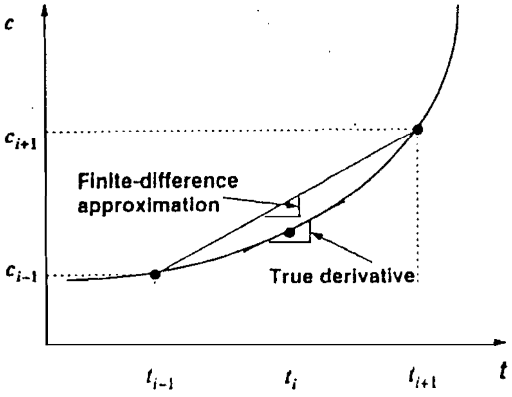


FIGURE 2.5
Numerical differentiation.

centered difference can be employed (Fig. 2.5):

$$\frac{dc_i}{dt} \cong \frac{\Delta c}{\Delta t} = \frac{c_{i+1} - c_{i-1}}{t_{i+1} - t_{i-1}} \tag{2.23}$$

Although this is certainly a valid approximation, numerical differentiation is an inherently unstable operation — that is, it amplifies errors. As depicted in Fig. 2.6, because the finite differences (Eq. 2.23) are subtractive, random positive and negative errors in the data are additive. As described in the following example, a technique known as equal-area differenriation can be used to moderate this problem (Fogler 1986).

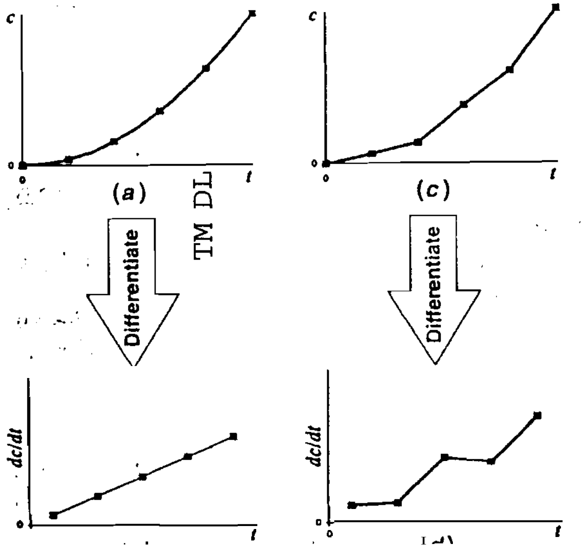


FIGURE 2.6
Illustration of how even small data errors are amplified by numerical differentiation. (a) Data with no error; (b) the resulting numerical differentiation; (c) data modified slightly; (d) the resulting differentiation manifesting increased variability (reprinted,

EXAMPLE 2.2. DIFFERENTIAL METHOD. Use the differential method to evaluate the order and the constant for the data from Example **2.1.** Use equal-area differentiation to smooth the derivative estimates.

Solution: The data from Example **2.1** can be differentiated numerically to yield the estimates in Table **2.2.** The derivative estimates can be graphed as a bar chart (Fig. **2.7).** Then a smooth curve can be drawn that best approximates the area under the histogram. In other words try to balance out the histogram areas above and below the drawn curve. Then the derivative estimates at the data points can be read directly from the curve. These are listed in the last column of Table 2.2. Figure 2.8 shows a plot of the log of the negative derivative versus the log of concentration. The best-fit line for this case is

$$\log\left(-\frac{dc}{dt}\right) = -1.049 + 1.062 \log c \qquad (r^2 = 0.992)$$

TABLE 2.2
Data analysis to determine derivative estimates from time series of concentration

t (d)	c (mg L^{-1})	$-\frac{\Delta c}{\Delta t}$ (mg L^{-1} d^{-1})	$-\frac{dc}{dt}$ (mg L^{-1} d^{-1})
0	12.0		1.25
		1.3	
1	10.7		1.1
		0.85	
3	9.0		0.9
		0.95	
5	7.1		0.72
		0.50	
10	4.6		0.45
		0.42	
15	2.5		0.27
		0.14	
20	1.8		0.15

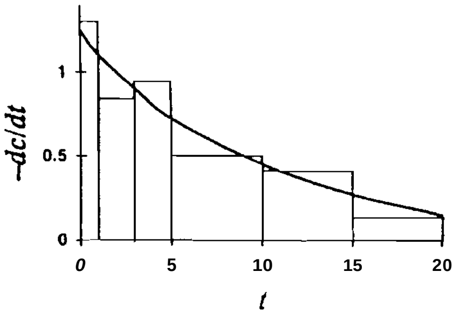


FIGURE 2.7
Equal-area differentiation.

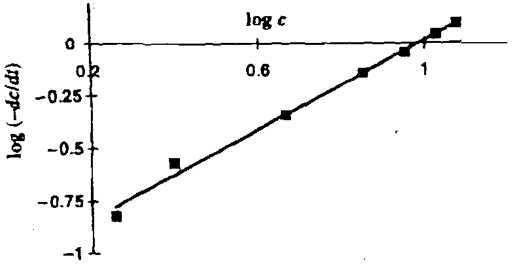


FIGURE 2.8
Plot of $\log(-dc/dt)$ versus $\log c$.

Therefore the estimates of the model parameters are

$$n = 1.062$$

$$k = 10^{-1.049} = 0.089\,\mathrm{d}^{-1}$$

Thus the differential approach suggests that a first-order model is a valid approximation.

2.2.3 The Method of Initial Rates

There are cases where reactions occur in which complications arise over time. For example a significant reverse reaction might occur. Further some reactions are very slow and the time required for the complete experiment might be prohibitive. For such cases the method of initial rates uses data from the beginning stages of the experiment to determine the rate constant and order.

In this method a series of experiments is carried out at different initial concentrations c_0. For each experiment, the initial rate $-dc_0/dt$ is determined by differentiating the data and extrapolating to zero time. For the case where the rate law follows Eq. 2.7, the differential method [that is, a plot of $\log(-dc_0/dt)$ versus $\log c_0$] can be used to estimate k and n. How this is accomplished can be illustrated by taking the logarithm of the negative of Eq. 2.7:

$$\log\left(-\frac{dc_0}{dt}\right) = \log k + n \log c_0 \tag{2.24}$$

Thus the slope provides an estimate of the order, whereas the intercept provides an estimate of the logarithm of the rate.

2.2.4 The Method of Half-Lives

The *half-life* of a reaction is the time it takes for the concentration to drop to one-half of its initial value. In other words

$$c(t_{50}) = 0.5c_0 \tag{2.25}$$

where t_{50} = half-life. Again we use Eq. 2.7 as our rate law model. If $c = c_0$ at $t = 0$, Eq. 2.7 can be integrated to give

$$t = \frac{1}{kc_0^{n-1}(n-1)}\left[\left(\frac{c_0}{c}\right)^{n-1} - 1\right] \tag{2.26}$$

If Eq. 2.25 is combined with 2.26, the result is

$$t_{50} = \frac{2^{n-1}-1}{k(n-1)}\frac{1}{c_0^{n-1}} \tag{2.27}$$

Taking the logarithm of this equation provides a linear relationship,

$$\log t_{50} = \log\frac{2^{n-1}-1}{k(n-1)} + (1-n)\log c_0 \tag{2.28}$$

Thus a plot of the log of the half-life versus the log of the initial concentration will yield a straight line with a slope of $1 - n$ (providing, of course, that Eq. **2.7** holds). The estimate of n can then be used in conjunction with the intercept to evaluate k.

It should be noted that the choice of a half-life is arbitrary. In fact we could have picked any other response time t_ϕ, where ϕ is the percent reduction. For this general case, Eq. 2.27 becomes

$$t_\phi = \frac{[100/(100-\phi)]^{n-1}-1}{k(n-1)}\frac{1}{c_0^{n-1}} \tag{2.29}$$

2.2.5 The Method of Excess

When a reaction involves many reactants, it is often possible to add excess quantities of all but one of the reactants. In such cases the reaction will depend solely on the single scarce reactant. For example several decomposition reactions for toxic substances (such as biodegradation and hydrolysis) can sometimes be represented by the reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \text{products} \tag{2.30}$$

where A = the toxic compound and B = another quantity (such as bacteria or hydrogen ion) that participates in the reaction. The following simple rate expression is often employed to model the reaction:

$$\frac{dc_a}{dt} = -kc_ac_b \tag{2.31}$$

where c_a and c_b = concentrations of the two reactants. If the initial concentration of B (c_{b0}) is much greater than A (c_{a0}), the ensuing reaction can have a measurable effect on **A** whereas B will be affected minimally. Consequently the reaction can be reformulated as

$$\frac{dc_a}{dt} = -(kc_{b0})c_a = -k_{b2}c_a$$

where $k_{b2} = kc_{b0}$ = a pseudo-first-order reaction rate. The other techniques described in the previous sections can then be employed to evaluate the coefficients.

2.2.6 Numerical and Other Methods

Aside from the foregoing approaches, there are computer-oriented methods for evaluating rate data. The ***integral/least-squares method*** offers the benefits of both the integral and differential approaches in a single method. In this approach, values are assumed for the parameters (n and k) and Eq. 2.7 is solved for $c(t)$. However, rather than by calculus, the solution is obtained numerically. The solution consists of a table of predicted concentrations corresponding to the measured values. The sum of the squares of the residuals between the measured and predicted concentrations can be calculated. The assumed values of n and k are then adjusted until a minimum or least-squares condition is reached. This can be done by trial-and-error. However, modern software tools such as spreadsheets include nonlinear optimization algorithms that provide an automated way to accomplish the same goal.

The final parameter values represent the n and k that correspond to a best-fit of the data. Thus the technique has the advantage of the integral technique in the sense that it is not overly sensitive to data errors. Further it has the benefit of the differential approach in that no a priori assumption of reaction order is required.

EXAMPLE 2.3. INTEGRAL LEAST-SQUARES METHOD. Use the integral least-square method to analyze the data from Example 2.1. Use a spreadsheet to perform the calculation.

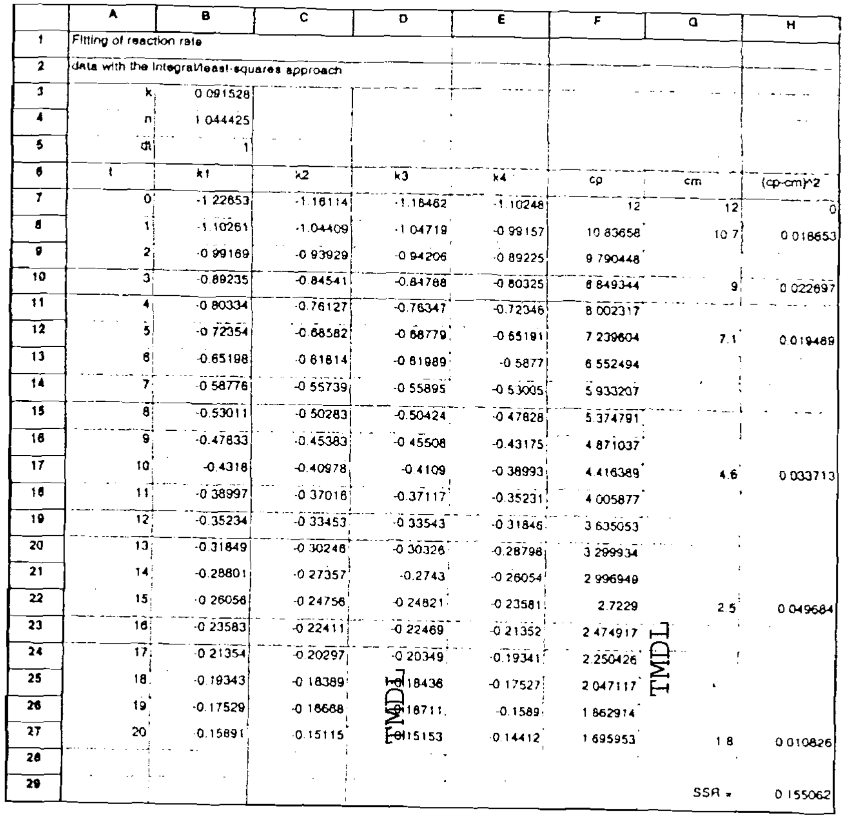
Solution: The solution to this problem is shown in Fig. 2.9. The Excel spreadsheet was used to perform the computation. Similar calculations can be implemented with other popular packages such as Quattro Pro and Lotus 123.

Initial guesses for the reaction rate and order are entered into cells B3 and B4, respectively, and the time step for the numerical calculation is typed into cell B5. For this case a column of calculation times is entered into column A starting at 0 (cell A7) and ending at 20 (cell A27). The k_1 through k_4 coefficients of the fourth-order RK method (see Lec. 7 for a description of this method) are then calculated in the block B7..E27. These are then used to determine the predicted concentrations (the c_p values) in column F. The measured values (c_m) are entered in column G adjacent to the corresponding predicted values. These are then used in conjunction with the predicted values to compute the squared residual in column H. These values are summed in cell H29.

At this point each of the spreadsheets determines the best fit in a slightly different way. At the time of this book's publication, the following menu selections would be made on Excel (v. 5.0). Quattro Pro (v. 4.5) and 123 for Windows (v. 4.0):

Excel or 123: t(ool) s(olver)   QP: t(ool) o(ptimizer)

Once you have accessed the solver or optimizer, you are prompted for a target or solution cell (H29), queried whether you want to maximize or minimize the target cell (minimize), and prompted for the cells that are to be varied (B3..B4). You then activate the algorithm [s(olve) or g(o)], and the results are as in Fig. 2.9. As shown, the values in cells B3..B4 minimize the sum of the squares of the residuals (SSR = 0.155) between the



	A	B	C	D	E	F	G	H
1	Fitting of reaction rate							
2	data with the integral/least-squares approach							
3	k	0.091528						
4	n	1.044425						
5	dt	1						
6	t	k1	k2	k3	k4	cp	cm	(cp-cm)^2
7	0	-1.22653	-1.16114	-1.16462	-1.10248	12	12	0
8	1	-1.10261	-1.04409	-1.04719	-0.99157	10.83658	10.7	0.018653
9	2	-0.99169	-0.93929	-0.94206	-0.89225	9.790448		
10	3	-0.89235	-0.84541	-0.84788	-0.80325	8.849344	9	0.022697
11	4	-0.80334	-0.76127	-0.76347	-0.72346	8.002317		
12	5	-0.72354	-0.68582	-0.68779	-0.65191	7.239604	7.1	0.019489
13	6	-0.65198	-0.61814	-0.61989	-0.5877	6.552494		
14	7	-0.58776	-0.55739	-0.55895	-0.53005	5.933207		
15	8	-0.53011	-0.50283	-0.50424	-0.47828	5.374791		
16	9	-0.47833	-0.45383	-0.45508	-0.43175	4.871037		
17	10	-0.4318	-0.40978	-0.4109	-0.38993	4.416389	4.6	0.033713
18	11	-0.38997	-0.37016	-0.37117	-0.35231	4.005877		
19	12	-0.35234	-0.33453	-0.33543	-0.31846	3.635053		
20	13	-0.31849	-0.30246	-0.30326	-0.28798	3.299934		
21	14	-0.28801	-0.27357	-0.2743	-0.26054	2.996949		
22	15	-0.26056	-0.24756	-0.24821	-0.23581	2.7229	2.5	0.049684
23	16	-0.23583	-0.22411	-0.22469	-0.21352	2.474917		
24	17	-0.21354	-0.20297	-0.20349	-0.19341	2.250426		
25	18	-0.19343	-0.18389	-0.18436	-0.17527	2.047117		
26	19	-0.17529	-0.16668	-0.16711	-0.1589	1.862914		
27	20	-0.15891	-0.15115	-0.15153	-0.14412	1.695953	1.8	0.010826
28								
29							SSR =	0.155062

FIGURE 2.9
The application of the integral least-squares method to determine the order and rate coefficient of reaction data. This application was performed with the Excel spreadsheet.

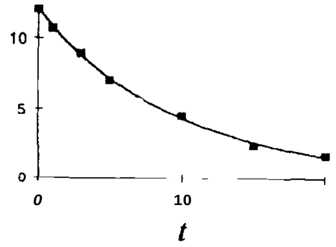


FIGURE 2.10
Plot of fit generated with the integral/least-squares approach.

There are a variety of other approaches for analyzing rate data beyond the ones

TMDL

presentations of Fogler (1986) and Grady and Lim (1980) for additional information. I will be reviewing some additional rate laws in later sections of this text Methods for evaluating their rate constants will be reviewed in a "just-in-time" fashion as they are needed.

2.3 STOICHIOMETRY

In the previous lecture I introduced the notion of mass concentration as a means to quantify the strength of a single chemical compound in water. Now that we are dealing with reactions, several compounds may react to form other compounds. Therefore we might want to determine "how much" of a reactant or product is consumed or created as the reaction proceeds. The answer to this question resides in the ***stoichiometry***, or number of moles, taking part in a reaction.

For example the decomposition or oxidation of sugar is represented by (recall Eq. *2.3)*

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \tag{2.33}$$

This equation specifies that 6 moles of oxygen will react with 1 mole of glucose to form 6 moles of carbon dioxide and 6 moles of water. In later lectures we directly use molar concentrations when we mathematically manipulate such equations to solve chemical equilibrium problems. For the time being, as outlined in the previous lecture. we must be able to interpret Eq. 2.33 from a mass-concentration perspective.

First, let's understand how the glucose in Eq. 2.33 would be expressed in mass units. This is usually done in two ways. The most direct way is to express the concentration on the basis of the whole molecule. For example we might say that a beaker contained 100 g m^{-3} as glucose. This is often abbreviated as 100 g-glucose m^{-3}. The number of moles of glucose in this solution can be determined with the gram molecular weight of glucose. The gram molecular weight can be calculated as

	Number of moles		**Mass of one mole**		
$6 \times C$ =	6	×	12 g	=	72 g
$12 \times H$ =	12	×	1 g	=	12 g
$6 \times O$ =	6	×	16 g	=	96 g
	Gram molecular weight			=	180 g

This result can be used to compute the molar concentration,

$$100\frac{\text{g-glucose}}{\text{m}^3}\left(\frac{1 \text{ mole}}{180 \text{ g-glucose}}\right) = 0.556 \text{ mole m}^{-3} \tag{2.34}$$

An alternative is to express the concentration in terms of the mass of one of the components of glucose. Because it is an organic carbon compound. glucose could be expressed as g m^{-3} of carbon. For example

$$\text{g-glucose}\left(\frac{6 \text{ moles C} \times 12 \text{ gC/mole C}}{}\right) = 40 \text{ gC m}^{-3} \tag{2.35}$$

Thus 100 g-glucose m^{-3} corresponds to 40 g m^{-3} of organic carbon, or 40 gC m^{-3}.

Such conversions are often expressed as stoichiometric ratios. For example the mass of carbon per mass of glucose can be expressed as

$$a_{cg} = \frac{6 \text{ moles C} \times 12 \text{ gC/mole C}}{180 \text{ g-glucose}} = 0.4 \text{ gC g-glucose}^{-1} \tag{2.36}$$

where a_{cg} = stoichiometric ratio of carbon to glucose This ratio can be used to formulate Eq. 2.35 alternatively as

$$c_c = a_{cg}c_g = 0.4\frac{\text{gC}}{\text{g-glucose}}\left(100\frac{\text{g-glucose}}{\text{m}^3}\right) = 40 \text{ gC m}^{-3} \tag{2.37}$$

where the subscripts c and *g* designate carbon and glucose, respectively.

Aside from calculating how much individual element is contained in a molecule, stoichiometric conversions are often used to determine how much of a reactant or product is consumed or produced by a reaction. For example how much oxygen would be consumed if 40 gC m^{-3} of glucose reacted according to Eq. 2.33? First, we can calculate the mass of oxygen consumed per mass of glucose carbon decomposed,

$$r_{oc} = \frac{6 \text{ moles } O_2 \times 32 \text{ gO/mole } O_2}{6 \text{ moles C} \times 12 \text{ gC/mole C}} = 2.67 \text{ gO gC}^{-1} \tag{2.38}$$

where r_{oc} = mass of oxygen consumed per carbon decomposed. This ratio can be used *to* determine

$$2.67\frac{\text{gO}}{\text{gC}}\left(40\frac{\text{gC}}{\text{m}^3}\right) = 106.67 \text{ gO m}^{-3} \tag{2.39}$$

Thus if 40 gC m^{-3} of glucose (or 100 g-glucose m^{-3}) is decomposed, 106.67 gO m^{-3} will be consumed.

EXAMPLE 2.4. STBICHIOMETRIC RATIOS. Aside from the decomposition of organic carbon compounds such as glucose, other reactions consume oxygen in natural waters. One such process, called ***nitrification***, involves the conversion of ammonium (NH_4^+) to nitrate (NO_3^-). Although we will learn in Lec. 23 that it's a little more complicated, the nitrification reaction can be represented by

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + H_2O + NO_3^-$$

Suppose you are told that a beaker contains 12 g-ammonium m^{-3} is nitrified according to the first-order reaction

$$\frac{dn_a}{dt} = -k_n n_a$$

where n_a = ammonium concentration and k_n = first-order rate constant for nitrification. (*a*) Convert the concentration to gN m^{-3}. (*b*) Determine how much oxygen is consumed if the nitrification reaction goes to completion. (*c*) Calculate the rate of oxygen consumption

Solution: (a)

$$12\frac{\text{gNH}_4^+}{\text{m}^3}\left(\frac{1 \times 14 \text{ gN}}{1 \times 14 + 4 \times 1 \text{ gNH}_4^+}\right) = 9.33 \text{ gN m}^{-3}$$

(b)

$$r_{on} = \frac{32}{1 \times 14} = 4.57 \text{ gO gN}^{-1}$$

Therefore 4.57 gO are taken up for every gN that is nitrified. For our example.

$$9.33\frac{\text{gN}}{\text{m}^3}\left(4.57\frac{\text{gO}}{\text{gN}}\right) = 42.67 \text{ gO m}^{-3}$$

(c) At the onset of the experiment, the ammonium concentration will be at 9.33 gN m^{-3}. Using the oxygen-to-nitrogen ratio, the initial rate of oxygen consumption can be calculated as

$$\frac{\quad}{dt} = -r_{on}k_n n_o = -4.57\frac{\text{gO}}{\text{gN}}(0.1 \text{ d}^{-1})\left(9.33\frac{\text{gN}}{\text{m}^3}\right) = -4.264 \text{ gO m}^{-3} \text{ d}^{-1}$$

2.4 TEMPERATURE EFFECTS

The rates of most reactions in natural waters increase with temperature. A general rule of thumb is that the rate will approximately double for a temperature rise of 10°C.

A more rigorous quantification of the temperature dependence is provided by the ***Arrhenius* equation.**

$$k(T_a) = Ae^{\frac{-E}{RT_a}} \tag{2.40}$$

where A = a preexpanential or frequency factor
E = activation energy (J mole-')
R = the gas constant (8.314 J mole^{-1} K^{-1})
T_a = absolute temperature (K)

Equation 2.40 is often used to compare the reaction rate constant at two different temperatures. This can be done by expressing the ratio of the rates, as in

$$\frac{k(T_{a2})}{k(T_{a1})} = e^{\frac{E(T_{a2} - T_{a1})}{RT_{a2}T_{a1}}} \tag{2.41}$$

Equation 2.41 can be simplified by realizing that:

- Because temperatures in most water bodies vary over a rather narrow range *(273* to 313 K), the product of T_{a1} and T_{a2} is relatively constant.
- The difference in temperature ($T_{a2} - T_{a1}$) is identical whether an absolute or a centigrade scale is used.

Consequently the following can be defined as a constant:

$$\theta \equiv e^{\frac{E}{RT_{a2}T_{a1}}} \tag{2.42}$$

TABLE 2.3
Some typical values of θ used in water-quality modeling

θ	Q_{10}	**Reaction**
1.024	1.27	Oxygen reaeration
1.047	1.58	BOD decomposition
1.066	1.89	Phytoplankton growth
1.08	2.16	Sediment oxygen demand (SOD)

$$\frac{k(T_2)}{k(T_1)} = \theta^{T_2 - T_1} \tag{2.43}$$

where the temperature is expressed in °C.

In water-quality modeling, many reactions are reported at 20°C (see Prob. *216)*. Therefore, Eq. 2.43 is usually expressed as

$$k(T) = k(20)\theta^{T-20} \tag{2.44}$$

Table 2.3 summarizes some commonly used values for θ. Figure 2 11 illustrates; the functional dependency on temperature across the range commonly encountered. in natural waters.

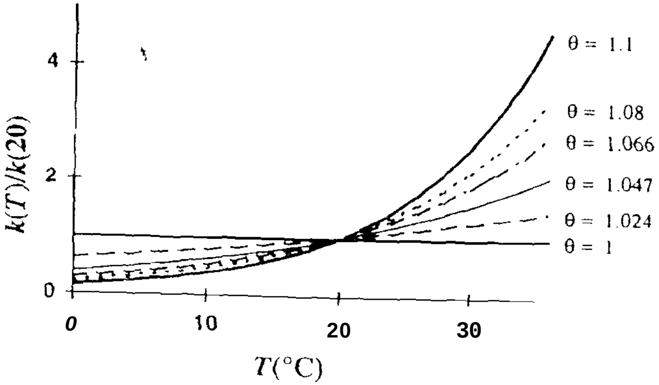
The temperature dependence of biologically mediated reactions is often expressed as the quantity Q_{10}, which is defined as the ratio

$$Q_{10} = \frac{k(20)}{k(10)} \tag{2.45}$$

Substituting Eq. 2.44 yields

$$Q_{10} = \theta^{10} \tag{2.46}$$

Note that **Eq.** 2.46 can be used to compute that a Q_{10} of *2* (recall the heuristic at the beginning of this section) is equivalent to a θ of $2^{0.1}$ = 1.072. Thus a θ = 1.072 corresponds to a doubling of the rate for a temperature rise from 10 to 20°C.



۴۱

FIGURE 2.11

EXAMPLE 2.5. EVALUATION OF TEMPERATURE DEPENDENCY OF REACTIONS. A laboratory provides you with the following results for a reaction:

$$T_1 = 4°C \qquad k_1 = 0.12\ d^{-1}$$

$$T_2 = 16°C \qquad k_2 = 0.20\ d^{-1}$$

(*a*) Evaluate θ for this reaction.

(*b*) Determine the rate at 20°C.

Solution: (a) To evaluate this information, we can take the logarithm of Eq. 2.43 and raise the result to a power of 10 to give

$$\theta = 10^{\frac{\log k(T_2) - \log k(T_1)}{T_2 - T_1}}$$

Substituting the data gives

$$\theta = 10^{\frac{\log 0.12 - \log 0.20}{4-16}} = 1.0435$$

(*b*) Equation 2.43 can then be used to compute

$$k(20) = 0.20 \times 1.0435^{20-16} = 0.237\ d^{-1}$$

Finally it should be noted that there are some reactions that do not follow the Arrhenius equation. For example certain biologically mediated reactions shut down at very high and very low temperatures. The formulations used in such situations are introduced in later lectures.

PROBLEMS

2.1. You perform a series of batch experiments and come up with the following data:

t (hr)	0	2	4	6	8	10
c (μg L^{-1})	10.5	5.1	3.1	2.8	2.2	1.9

Determine the order (n) and the rate (k) of the underlying reaction.

2.2. Derive a graphical approach to determine whether a reaction is third-order.

2.3. To study the photodegradation of aqueous bromine, we dissolved a small quantity of liquid bromine in water, placed it in a clear jar, and exposed it to sunlight. The following data were obtained:

t (min)	10	20	30	40	50	60
c (ppm)	3.52	2.48	1.75	1.23	0.87	0.61

whether the reaction is zero-, first-, or second-order and estimate the reaction rate.

[illegible] have a more complete data Set than

T (°C)	4	8	12	16	20	24	28
k (d^{-1})	0.120	0.135	0.170	0.200	0.250	0.310	0.360

Use this data to estimate θ and k at 20°C

2.5. An article in a limnological[1] journal reports a Q_{10} for a phytoplankton growth rate of 1.9. If the growth rate is reported as 1.6 d^{-1} at 20°C, what is the rate at 30°C?

2.6. You set up a series of 300-mL bottles and add 10 mL of a glucose solution to each. Note that the glucose solution has a concentration of 100 mgC L^{-1}. To each bottle you add a small quantity (that is, with an insignificant amount of carbon compared to the glucose) of bacteria. You fill the remainder of their volumes up with water. Finally you seal each bottle and incubate them at 20°C. At various times you open one of the bottles and measure its oxygen content. The following data results:

t (d)	0	2	5	10	20	30	40	50	60	70
c (mgO$_2$ L^{-1})	10	8.4	6.5	4.4	2.3	1.6	1.3	1.2	1.1	1.1

(*a*) Develop a conceptual model for what is taking place inside the bottle.

(*b*) Using the information from this lecture, attempt to estimate the decay rate for the glucose.

2.7. In the fall of 1972 Larsen et al. (1979) measured the following concentrations of total phosphorus in Shagawa Lake, Minnesota:

Day	mg m^{-3}	Day	mg m^{-3}	Day	mg m^{-3}
250	97	270	72	290	62
254	90	275	51	295	55
264	86	280	57	300	46

It is known that the primary reason for the reduction in concentration during this period was the settling of particulate phosphorus. If the lake is assumed to acr as a batch reactor and settling is assumed to follow a first-order process, determine the removal rate of total phosphorus for the lake. If the lake's mean depth is 5.5 m, calculate the settling velocity for total phosphorus.

2.8. Population dynamics is important in predicting how human development of a watershed might influence water quality. One of the simplest models incorporates the assumption that the rate of change of the population p is proportional to the existing population at any time t:

$$\frac{dp}{dt} = Gp \qquad \text{(P2.8)}$$

۳۲

---

[1] Limnology is the study of lakes. The terminology is derived from the Greek word for lake: *limnos*

where G = the growth rate (yr^{-1}). Suppose that census data provides the following trend in population of a small town over a 20-yr period:

t	1970	1975	1980	1985	1990
p	100	212	448	949	2009

If the model (Eq. P2.8) holds. estimate G and the population in 1995.

2.9. The world took about 300 years to grow from about 0.5 billion to 4 billion people. Assuming first-order growth, determine the growth rate. Estimate the population over the next century if this rate continues.

2.10. Many lakes in temperate regions are thermally stratified in the summer, consisting of an upper layer (epilimnion) and a lower layer (hypolimnion). In general the surface layer has dissolved oxygen concentration near saturation. If it is productive (that is, has high plant growth), settling plant matter can collect in the hypolimnion. The decomposition of this matter can then lead to severe oxygen depletion in the bottom waters. When turnover occurs in the fall (that is, vertical mixing due to decreasing temperature and increasing winds), the mixing of the two layers can result in the lake's having an oxygen concentration well below saturation. The following data were collected for Onondaga Lake in Syracuse, New York:

Date	Sep. 30	Oct. 3	Oct. 6	Oct. 9	Oct. 12	Oct. 15	Oct. 18	Oct. 21
Oxygen conc. ($mg\ L^{-1}$)	4.6	6.3	7.3	8.0	8.4	8.7	8.9	9.0

If the saturation concentration is 9.2, use this data to evaluate a first-order reaeration rate for the system (units of d^{-1}). Assume that the lake acts as an open batch reactor; that is, ignore inflows and outflows of oxygen except gas transfer across the lake's surface. Also, express the rate as a transfer velocity (units of $m\ d^{-1}$). Note that Onondaga Lake has a surface area of 11.7 km^2 and a mean depth of 12 m.

2.11. A reaction has a Q_{10} of 2.2. If the reaction rate at 25°C is 0.853 wk^{-1}, what is the reaction rate at 15°C?

2.12. A commonly used anesthetic is absorbed by human body organs at a rate proportional to its concentration in the bloodstream. Assume that a patient requires 10 mg of the anesthetic per kg of body weight to maintain an acceptable level of anesthesia for surgery. Compute how many mg must be administered to a 50-kg patient to maintain a proper level for a 2.5-hr operation. Assume that the anesthetic can be introduced into the patient's bloodstream as a pulse input and that it decays at a rate of 0.2% per minute.

2.13. Estimate the age of the fossil remains of a skeleton with 2.5% of its original carbon-14 content. Note that carbon-14 has a half-life of 5730 yr.

2.14. In 1828 Friedrich Wohler discovered that the inorganic salt ammonium cyanate (NH_4OCN) can be converted into the organic compound urea (NH_2CONH_2), as in

$$NH_4OCN\ (aq) \rightarrow NH_2CONH_2\ (aq)$$

The proof that this reaction occurred marked the beginning of modern organic and bio- [illegible] the following data for an experiment initially

Time (min)	0	20	50	65	150
NH_4OCN ($mole\ L^{-1}$)	0.381	0.264	0.180	0.151	0.086

Determine the order and rate of the reaction.

2.15. You perform a batch experiment and develop the following data:

t	0	2	4	6	8	10
c	10.0	8.5	7.5	6.7	6.2	5.8

You know from experience that the reaction should be following a third-order reaction. Use this information and the integral method to determine a value for the reaction rate.

2.16. Suppose that the temperature dependence of a reaction rate is based on its value at 25°C (note that this is the convention in areas such as chemical engineering). For example

$$k(T) = 0.1(1.06)^{T-25}$$

Reexpress this relationship based on the rate's value at 20°C.

2.17. The following data for concentrations and times were developed for a series of batch experiments having different initial conditions:

t	c			
0	1.00	2.00	5.00	10.00
1	0.95	1.87	4.48	8.59
2	0.91	1.74	4.04	7.46

Assuming that Eq. 2.7 holds, use the method of initial rates to determine the order and rate of the reaction.

2.18. Assuming that Eq. 2.7 holds, use the method of half-lives to determine the reaction order and rate by evaluating the following half-lives and initial concentrations developed from a series of batch experiments:

c_0	1	2	5	10
t_{50}	16	11	7	5

2.19. Assuming that Eq. 2.7 holds, use the integral least-squares method to determine the reaction order and rate by evaluating the following data collected from a batch experiment:

t	0	2	4	6	8	10
c	10	7.5	5.8	4.6	3.8	3.1

2.20. The concentration of inorganic phosphorus in natural waters is usually expressed as phosphorus (P). However, it is sometimes expressed as phosphate (PO_4). When reading a scientific article, you see that an estuary has an inorganic phosphorus concentration of

10 mg m^{-3}. As is sometimes the case no guidance is given regarding how the concentration is expressed. How does the concentration change if it is actually mgPO$_4$ m^{-3}? By what factor would you be off?

2.21. A more complete representation of the decomposition reaction is provided by

$$C_{106}H_{263}O_{110}N_{16}P_1 + 107O_2 + 14H^+ \rightarrow 106CO_2 + 16NH_4^+ + HPO_4^{2-} + 108H_2O$$

In contrast to the simplified version in Eq. 2.3, this reaction reflects that organic matter contains the nutrients nitrogen (N) and phosphorus (P). On the basis of this equation, given that 10 gC m^{-3} of organic matter is decomposed, calculate

(*a*) the stoichiometric ratio for the amount of oxygen consumed per carbon decomposed, r_{oc} (gO gC^{-1})
(*b*) the amount of oxygen consumed (gO m^{-3})
(*c*) the amount of ammonium released (expressed as mgN m^{-3})