ENV 5666 – Water Quality Management

Lecture 2

Fundamentals of Reaction Kinetics and Rates

Reaction Kinetics & Rates

- Quantitative definition of the rate of transformation (appearance or disappearance) of a contaminant (e.g., Hg) or indicator (e.g., BOD) in an aquatic environment.
- Found theoretically from the stoichiometry of chemical reactions (if available) or experimentally (mostly in laboratory-controlled conditions).

Reaction Types

- Heterogeneous reaction (i.e., one, two or three phases)
- Homogeneous reaction (i.e., only one phase)
- Reversible reaction ($A \leftrightarrow B$): Equilibrium Chemistry
- Irreversible reaction ($A \rightarrow B$): Main focus on single direction with rate of disappearance of a reactant

Reaction Kinetics

Law of Mass Action:

"rate of transformation is proportional to the concentration of reactants ", as follows:

$$\alpha A + \beta B + \ldots \rightarrow \text{products}$$

$$dc_A/dt = -\,k\, f(c_A, \ldots c_I, \ldots) = -\,k\, c_A^{\alpha}\, c_B^{\beta} = -\,kc_A^{n}$$

c	=	concentration of a single reactant
n	=	$(\alpha + \beta)$ = order of reaction
k	=	reaction rate constant, a temperature-dependent rate constant

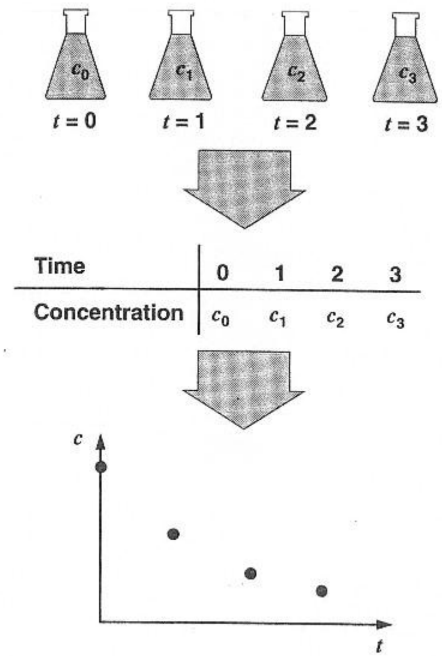


FIGURE 2.1
A simple experiment to collect rate data for a pollutant in a natural water.

Zero-Order Rate (n = 0)

$$dc/dt \;=\; -k$$

Which, for data obtained in an experiment in a batch reactor, is the conservation of mass statement (i.e., "*Rate of Accumulation = Rate of Transformation*").

Then, after integration over time and boundary conditions yields:

$$c = c_0 - kt$$

where:

$c = c_0$ at $t = 0$ and k has units of $ML^{-3}\,T^{-1}$

First-Order Rate (n = 1)

$$dc/dt = -kc$$

which, after integration of data obtained in a batch reactor experiment, becomes

$$\ln c - \ln c_0 = kt \quad \text{or}$$

$$c = c_0 e^{-kt}$$

where $c = c_0$ at $t = 0$ and k with units of T^{-1}

In other words, concentration halves every half-life.

Second-Order Rate (n = 2)

$$dc/dt \;=\; -kc^2$$

which after integration for data from a batch reactor experiment yields:

$$1/c \;=\; 1/c_0 + kt$$

where $c = c_0$ at $t = 0$ and k has units of $(M\,T)^{-1}L^{3}$

Methods to Quantify the Rate of Reaction, k

(all should be based on regression analysis or least-squares methods)

- Integral Method (Eq.2.7)
- Differential Method (Eq. 2.22)
- Method of Initial Rates (Eq. 2.24)
- Method of Half-lives (Eq. 2.29)
- Method of Excess (i.e., one reactant is in excess)
- Numerical Methods (i.e., hand calculations or computer programs, including MSExcel spreadsheets and regression options)

Temperature Effect On Rates

- Rates of most reactions in natural waters increase with temperature.
- Rate approximately double every 10°C of increase.
- Arrhenius Equation

$$\mathbf{k(T_a) = Ae^{(-E/RT_a)}}$$

where:

A = pre-exponential frequency factor

E = activation energy

R = the gas constant

T_a = absolute temperature

Comparison of Reaction Rate Constants at Two Different Temperatures

- $k(T_{a2}) / k(T_{a1}) = e^{E(T_{a2}-T_{a1})/R(T_{a2}-T_{a1})} \approx \theta^{(T_2-T_1)}$,

  where $\theta \approx E/(RT_{a2}T_{a1})$, because most temperature ranges are narrow (273-313K, 0 to 100 centigrade or 32 to 211 F)

Use of Rates Expressions

- In the quantitative representation of the "transformation" components (i.e., chemical or biological or both, for instance, decomposition, oxidation, reduction, hydrolysis, photolysis, chemical adsorption, etc.) in the conservation of mass statement!

Lecture 2- Example 2.1

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 $\ln c$ versus t most closely approximates a straight line. The best-fit line for this case is

$$\ln c = 2.47 - 0.0972t \qquad (r^2 = 0.995)$$

Therefore the estimates of the two model parameters are

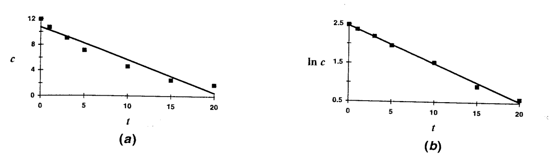
$$k = 0.0972\ \mathrm{d}^{-1}$$
$$c_0 = e^{2.47} = 11.8\ \mathrm{mg\ L}^{-1}$$

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

$$k' = \frac{0.0972}{2.3025} = 0.0422$$



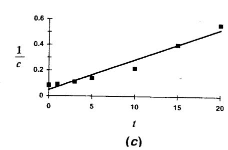


FIGURE 2.4
Plots to evaluate whether the reaction is (*a*) zero-order, (*b*) first-order, or (*c*) second-order.

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.

Lecture 2 – Example 2.2

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

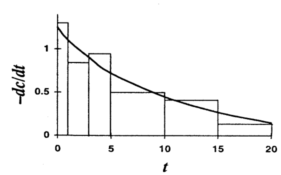


FIGURE 2.7
Equal-area differentiation.

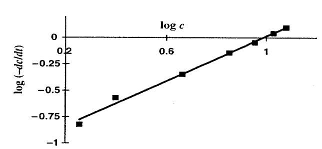


FIGURE 2.8
Plot of $\log(-dc/dt)$ versus $\log\ c$.

Therefore the estimates of the model parameters are

$$n = 1.062$$
$$k = 10^{-1.049} = 0.089\ \text{d}^{-1}$$

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

Lecture 2 – Example 2.3

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 predicted and measured data. Note how these coefficient values differ from Examples 2.1 and 2.2. A plot of the fit along with the data is shown in Fig. 2.10.

	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.

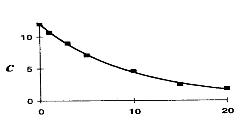


FIGURE 2.10
Plot of fit generated with the integral/least-squares approach.

Lecture 2 – Example 2.5

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

$$T_1 = 4°\text{C} \qquad k_1 = 0.12\ \text{d}^{-1}$$
$$T_2 = 16°\text{C} \qquad k_2 = 0.20\ \text{d}^{-1}$$

(*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

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