Web Appendix A.5: Using Semilog Plots in Rate Data Analysis

Semilog graph paper is used when dealing with either exponential growth or decay, such as

$$y = be^{mx} \tag{WA.5-1}$$

For the first-order elementary reaction

$$A \longrightarrow \text{Products}$$

which is carried out at constant volume, the rate of the disappearance of A is given by

$$\frac{-dC_A}{dt} = kC_A \tag{WA.5-2}$$

When $t = 0$, $C_A = C_{A0}$, where the units of C_A are g mol/dm^3; t is expressed in minutes; and k is expressed in reciprocal minutes. Integrating the rate equation, we obtain

$$\text{In}\frac{C_A}{C_{A0}} = -kt \tag{WA.5-3}$$

We wish to determine the specific reaction rate constant, k. A plot of ln C_A versus t should produce a straight line whose slope is $-k$. We may eliminate the calculation of the log of each concentration data point by plotting our data on semilog graph paper. The points in Table WA.5-1 are plotted on the semilog graph shown in Figure WA.5-1.

TABLE WA.5-1

t (min)	0	2	4	8	14
C_A (gmol/dm^3)	2.0	1.64	1.38	0.95	0.60

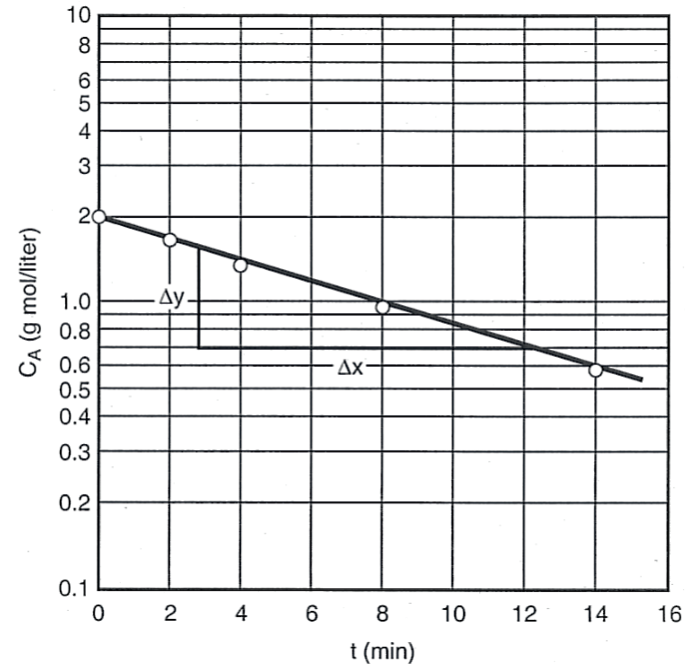

Figure WA.5-1

Algebraic Method. Draw the best straight line through your data points. Choose two points on this line, t_1 and t_2, and the corresponding concentrations C_{A1} and C_{A2} at these times:

$$\text{In}\frac{C_{A1}}{C_{A0}} = -kt_1 \qquad \text{In}\frac{C_{A2}}{C_{A0}} = -kt_2$$

$$\text{In}C_{A2} - \text{In}C_{A1} = -k(t_2 - t_1) \tag{WA.5-4}$$

Rearranging yields

$$k = -\frac{\text{In}C_{A2} - \text{In}C_{A1}}{t_2 - t_1} = \frac{\text{In}(C_{A2} / \text{In}C_{A1})}{t_2 - t_1} \tag{WA.5-5}$$

When t = 8, C_A = 1.05; when t = 12, C_A = 0.75. Substituting into Equation (WA.5-5) gives us

$$k = \frac{\text{In}(1.05/0.75)}{12 - 8\ \text{min}} = \frac{0.336}{4\ \text{min}}$$

$$= (0.084\ \text{min})^{-1}$$

Graphical Technique In the preceding example, we had

$$\mathrm{In}\frac{C_{A1}}{C_{A0}} = -kt_1 \tag{WA.5-6}$$

Dividing by 2.3, we convert to log base 10:

$$\frac{\mathrm{In}(C_A / C_{A0})}{2.3} = \log(C_A / C_{A0}) = \frac{-kt}{2.3}$$

The slope of a plot of log C_A versus time should be a straight line with slope $-k/2.3$. Referring to Figure WA.5-1, we draw a right triangle with the acute angles located at points $C_A = 1.6$, $t = 2.8$ and $C_A = 0.7$, $t = 12.8$. Next, the distances x and y are measured with a ruler. These measured lengths in y and x are 1.35 and 4.65 cm, respectively:

$$\Delta y = -1.35 \text{ cm} \times \frac{1 \text{ cycle}}{3.9 \text{ cm}} -0.35 \text{ cycle}$$

$$\Delta x = 4.65 \text{ cm} \times \frac{14 \text{ min}}{6.7 \text{ cm}} \; 9.7 \text{ min}$$

$$\text{slope} = \frac{-0.35}{9.7} -0.0361$$

$$\begin{aligned} k &= -2.3 \text{ (slope)} = -2.3 \, (-0.0361) \text{ min}^{-1} \\ &= 0.083 \text{ min}^{-1} \end{aligned}$$

A modification of the algebraic method is possible by drawing a line on semilog paper so that the dependent variable changes by a factor of 10. From Equation (WA.5-5) in the form

$$\begin{aligned} k &= \frac{\mathrm{In}(C_{A1}/C_{A2})}{t_2 - t_1} \\ &= \frac{2.3 \log (C_{A1}/C_{A2})}{t_2 - t_1} \end{aligned} \tag{WA.5-7}$$

choose the points (C_{A1}, t_1) and (C_{A2}, t_2) so that $C_{A2} = 0.1C_{A1}$:

$$k = \frac{2.3 \log 10}{t_2 - t_1} = \frac{2.3}{t_2 - t_1} \tag{WA.5-8}$$

This modification is referred to as the *decade method*.