

Homework #9c

solution outlines

from Averill text

- 27.** To determine which (elementary) step in a proposed mechanism is the rate-determining step, one must compare the rate expression for each step with the rate law for the overall reaction. The step that has the same rate law, differing only in the expression of k , is the rate-determining step. Example 14.12 and Exercise 14.12 show the case for $k = k_1$. (Note that for mechanisms that involve more than two steps, the k for the overall rate law may be a product of several k 's, such as $k = k_1k_2$ or many other more complex possibilities.)
- 30.** Activation energy E_a is the amount of energy that particles must have in order to react when they collide, allowing them to overcome electrostatic repulsion and providing sufficient energy to break bonds in the reactant molecules. It is a more relevant energy to the kinetics of a reaction than average kinetic energy of the particles in that it is a crucial part of the Arrhenius equation, Equation 14.43. It helps to indicate which collisions are *effective at producing a reaction*, not just the total number of collisions.

As discussed in Chapter 10 (see the *very* important Figure 10.14), an increase in temperature increases the average kinetic energy of the particles in a sample. Additionally, it increases the *distribution* of speeds and kinetic energies of the particles. Thus, at higher temperatures, there is a larger fraction of particles with energy greater than E_a . The curves at the right of Figure 14.19 show that, for a certain reaction, the fraction of molecules with energy greater than E_a is greater at 500K than at 300K. Thus, the number of reaction-producing collisions increases at higher T .

- 50.** The steps are elementary, so the exponents in the rate law are equal to the stoichiometric coefficients. Thus, we get

$$\text{rate}_1 = k_1 [\text{N}_2^1] [\text{O}_2]$$

$$\text{rate}_2 = k_2 [\text{O}_2^1] [\text{O}]$$

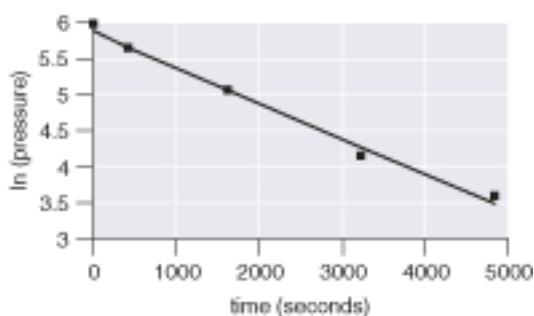
$$\text{rate}_3 = k_3 [\text{O}^1] [\text{N}_2]$$

The observed rate law for the overall reaction is equal to that of the rate-limiting (or rate-determining) step. Therefore, the first step is the rate-limiting step.

- 54.** Example 14.4 provides an example of this type of problem. Comparing Experiments 1 and 3 shows that doubling the benzoyl peroxide concentration increases the rate by a factor of 2 from

$(2.22 \times 10^{-4} M/s)/(1.12 \times 10^{-4} M/s) = 1.98 < 2$. Since the rate of reaction is directly proportional to the benzoyl peroxide concentration, this first data point indicates that the reaction is first-order. To make certain, we compare Experiments 1 and 4 to see that quadrupling the benzoyl peroxide concentration increases the rate by a factor of $(2.22 \times 10^{-4} M/s)/(0.59 \times 10^{-4} M/s) = 3.8$. This is not as close to four as we would like, so we compare Experiments 2 and 4 for which the concentration was increased by a factor of $0.70/0.25 = 2.8$ ongoing from Experiment 4 to Experiment 2. For a first order reaction, then, the rate should increase by this same factor. We find that the rate increases by a factor of $(1.64 \times 10^{-4} M/s)/(0.59 \times 10^{-4} M/s) = 2.8$. This value also indicates a first-order reaction. Thus, even without perfect data, we state that the reaction is very likely first-order with the rate law $\text{rate} = k[\text{benzoyl peroxide}]$.

- 58.** Table 14.6 indicates the various linear relationships that identify reaction order. Since the pressure is proportional to the concentration, we can plot the pressure, $\ln(\text{pressure})$, and $1/\text{pressure}$ versus the reaction time to see which is linear. You should confirm for yourself that only a plot of $\ln(\text{pressure})$ versus time gives a straight line. Thus, the reaction is first-order. The plot is below:



As in the text we determine the slope from any two points on the line by calculating $\Delta y/\Delta x$. (Linear regression, or the “least squares” method, which provides a “best-fit” line, can also be used.) The slope is

$$\text{slope} = \frac{Dy}{Dx} = \frac{\ln(156) - \ln(276)}{(16002 - 400)\text{s}} = -2.4753 \times 10^{-4} \text{ s}^{-1}$$

For a first order reaction the slope = $-k$, giving $k = 4.75 \times 10^{-4} \text{ s}^{-1}$. (Note that the above points are not all exactly on the best-fit line that we’ve drawn. The slope of this best fit line is

$-4.90 \times 10^{-4} \text{s}^{-1}$. Had we chosen the first and last data points to calculate $\Delta y/\Delta x$, we would have gotten a value much closer to the linear regression slope.) Now, the integrated rate law for a first-order reaction is $\ln[A] = \ln[A]_0 - kt$. Thus, using the properties of natural logarithms found in Essential Skills 6, we find the time to reach 105mmHg from

$$t = \frac{\ln\left(\frac{[A]_0}{[A]}\right)}{k} = \frac{\ln\left(\frac{348}{105}\right)}{4.753 \cdot 10^{-4} \text{ s}^{-1}} = 2520 \text{ seconds}$$

Note that we used the pressure values, not the concentrations, because the two are proportional. (With the best-fit slope, we get $t = 2450$ seconds.)

62. Since $t_{1/2} = 0.693/k$, the rate constant is given by

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.7 \text{ hr}} \left(\frac{1 \text{ hr}}{3600 \text{ sec}} \right) = 1.803 \cdot 10^{-5} \text{ s}^{-1}$$

With this information we can write the rate law: $\text{rate} = (1.80 \times 10^{-5} \text{s}^{-1})[\text{H}_2\text{O}_2]$. Thus, the initial rate of decomposition with $[\text{H}_2\text{O}_2]_i = 7.5 \times 10^{-3} \text{M}$ is

$$\text{rate} = \frac{1.803 \cdot 10^{-5}}{\text{s}} \left(\frac{7.53 \cdot 10^{-3} \text{ mol}}{\text{L}} \right) = 1.43 \cdot 10^{-7} \text{ M/s}$$

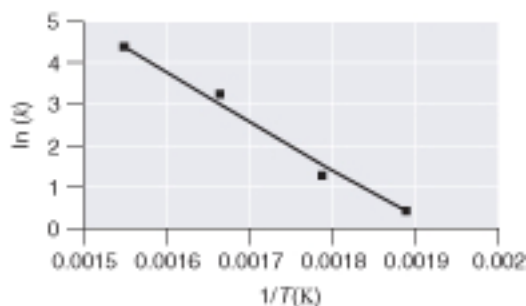
The integrated rate law for a first-order reaction is $[A] = [A]_0 e^{-kt}$, Equation 14.22. Thus, after 3.3hr $[A]$ is given by

$$[A] = [A]_0 \exp(-kt)$$

$$[A] = (7.53 \cdot 10^{-3} \text{ M}) \exp\left(-2 \frac{1.803 \cdot 10^{-5}}{\text{s}} \left(\frac{3600 \text{ s}}{1 \text{ hr}}\right) 3.3 \text{ hr}\right)$$

$$[A] = 6.13 \cdot 10^{-3} \text{ M}$$

71. From Equation 14.44, a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$. The plot is below, where the straight line is the linear regression, or “best-fit,” result.



The best-fit line gives a slope of $-1.2 \times 10^4 \text{ K}$. To two significant figures, the estimated slope using $\Delta y/\Delta x$ on the two endpoints is the same. *Note that the slope has a unit!* The activation energy is

$$E_a = 2 \left(1.23 \times 10^4 \text{ K} \right) \left(\frac{8.314 \text{ J}}{\text{K mol}} \right) = \frac{1.03 \times 10^5 \text{ J}}{\text{mol}} = 1.03 \times 10^2 \text{ kJ/mol}$$

81. To calculate the elapsed time, solve Equation 14.36 for t . This gives

$$t = \frac{2 \ln(N/N_0)}{k} = \frac{2 \ln(N/N_0)}{0.693/t_{1/2}} = \frac{2 t_{1/2} \ln(N/N_0)}{0.693}$$

The half-life for carbon-14 is 5730 yr. The ratio N/N_0 is obtained by noting that, if 24% of the carbon-14 is gone, then 76% of it remains. Thus, $N/N_0 = 0.76$. Therefore the time that has elapsed from when the cast iron specimen was made is

$$t = \frac{2 t_{1/2} \ln(N/N_0)}{0.693} = \frac{2 (5730 \text{ yr}) \ln(0.76)}{0.693} = 2300 \text{ yr}$$

Thus, the specimen was made approximately in $2300 - 2000 = 300 \text{ B.C.}$, affirming the archaeologist's prediction.

1. (a) To show that the reaction is first order try fitting the logarithm of concentration versus time. Least-squares analysis gives

$$\ln c = 0.831 - 7.21 \times 10^{-4} t$$

with a correlation coefficient of 0.998.

(b) The half-life is given by $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{7.21 \times 10^{-4}} = 961 \text{ s}$

- (c) To decrease the concentration to 25% of initial value would take 2 half-lives, since after $t_{1/2}$ the concentration would be 50% and after 2 $t_{1/2}$ it would be 50% of 50%. So the answer is $2 \times 961 \text{ s} = 1922 \text{ s}$.

2. (a) Radioactive decay is a 1st order reaction which can be modeled as

$$-\frac{dc}{dt} = kc \quad \text{or} \quad c = c_o e^{-kt}$$

With a little algebra we can get an expression for the relationship between time, t , and the instant value of the decay rate:

at any time, t , we can write $-\frac{dc}{dt} = kc = kc_o e^{-kt}$ ①

and at time zero $-\frac{dc}{dt} = kc_o$ ②

divide ① by ② to get $\frac{r_t}{r_o} = e^{-kt}$ ③, where to reduce clutter let $r = \frac{dc}{dt}$.

Take the logarithm of both sides of ③ and substitute $k = \frac{\ln 2}{t_{1/2}}$. With rearrangement this

gives $t = -\frac{t_{1/2}}{\ln 2} \cdot \ln \frac{r_t}{r_o}$ ④.

So, for the oldest specimen we would measure the minimum instant decay rate of 0.1 ± 0.1 disintegrations per minute per gram. Set this equal to r_t in ④ and solve for t to get 41585 ± 5730 years.

- (b) For the youngest specimen we would measure the maximum instant decay rate of 15.2 ± 0.1 disintegrations per minute per gram. Set this equal to r_t in ④ and solve for t to get 54 ± 54 years.

Note that although the experimental uncertainty remains constant at 0.1 disintegrations per minute per gram, because this is compared against a measurement that can vary from 15.3

down to undetectable, the derived uncertainty in time varies greatly from 54 years to 54 years, respectively.

3. Assume steady state.

$$J = -D \frac{\Delta c}{\Delta x}; \quad \therefore \Delta x = D \frac{\Delta c}{J} = \frac{3.091 \times 10^{-4} \frac{\text{cm}^2}{\text{s}} \times 1.5 \times 10^{19} \frac{\text{atom}}{\text{cm}^3}}{10^{-3} \frac{\text{mol}}{\text{cm}^2 \text{hr}} \times \frac{1 \text{ hr}}{3600 \text{ s}} \times 6.02 \times 10^{23} \frac{\text{atom}}{\text{mol}}} = 2.773 \times 10^{-2} \text{ cm}$$

4. A solution to Fick's second law for the given boundary conditions is:

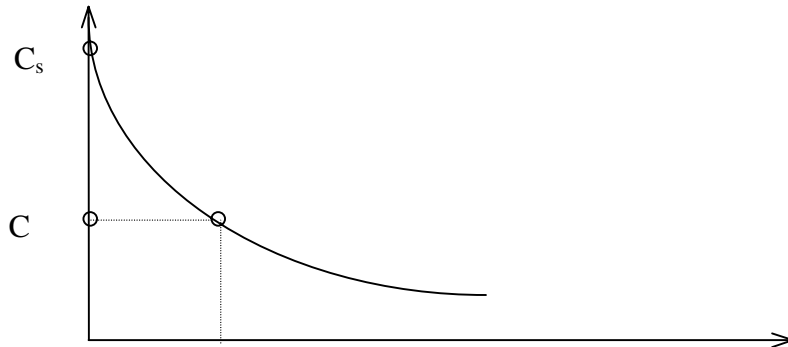
$$\frac{c}{c_s} = 1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}}, \quad \text{from which we get} \quad \operatorname{erf} \frac{x}{2\sqrt{Dt}} = 1 - 0.018 = 0.982$$

From the error function tables 0.982 is the *erf* of 1.67. This means that $\frac{0.002}{2\sqrt{Dt}} = \frac{0.001}{\sqrt{Dt}} = 1.67$

$$D = D_0 \cdot e^{\frac{-286 \cdot 10^5}{8.314 \cdot 1253}} = 6.45 \cdot 10^{-13} \frac{\text{cm}^2}{\text{sec}}$$

$$\therefore t = \frac{0.001^2}{1.67^2 \cdot 6.45 \cdot 10^{-13}} = 5.56 \cdot 10^5 \text{ sec} = 6.4 \text{ days}$$

5.



$$\frac{c}{c_s} = \operatorname{erfc} \frac{x}{2\sqrt{Dt}} = \operatorname{erfc} \frac{3 \times 10^{-3}}{2\sqrt{Dt}} = \operatorname{erfc}(2.083)$$

$$\frac{c}{c_s} = 1 - \operatorname{erf}(2.083), \quad \therefore 1 - \frac{c}{c_s} = 0.9964$$

$$\frac{c}{c_s} = 3.6 \times 10^{-3}, \quad \therefore c = 2.88 \times 10^{16} \text{ cm}^{-3}$$

The donor concentration in germanium is $2.88 \times 10^{16}/\text{cm}^3$.

$$\mathbf{6.} \quad c(x,t) = A + B \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad c(0,t) = c_s = A \quad c(x,0) = c_i = 0$$

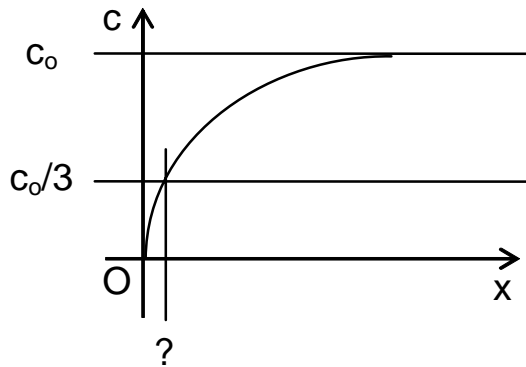
$$c(\infty,t) = c_i = 0 = A + B \rightarrow A = -B$$

$$\therefore c(x,t) = c_s - c_s \operatorname{erf} \frac{x}{2\sqrt{Dt}} = c_s \operatorname{erfc} \frac{x}{2\sqrt{Dt}} = 5 \times 10^{16} = c_s \operatorname{erfc} \frac{25 \times 10^{-4}}{2\sqrt{7.23 \times 10^{-9} \times 90 \times 60}}$$

$$\therefore c_s = \frac{5 \times 10^{16}}{\operatorname{erfc} \frac{25 \times 10^{-4}}{2\sqrt{7.23 \times 10^{-9} \times 5400}}} = 6.43 \times 10^{16} \text{ cm}^{-3}$$

$$\operatorname{erfc}(0.20) = 1 - \operatorname{erf}(0.20) = 1 - 0.2227 = \mathbf{0.7773}$$

5.



$$c = A + B \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad c(0,t) = 0 = A \quad c(\infty,t) = c_0 = B$$

$$\therefore c(x,t) = c_0 \operatorname{erf} \frac{x}{2\sqrt{Dt}}$$

What is x when $c = c_0/3$?

$$\frac{c_0}{3} = c_0 \operatorname{erf} \frac{x}{2\sqrt{Dt}} \Rightarrow 0.33 = \operatorname{erf} \frac{x}{2\sqrt{Dt}}; \operatorname{erf}(0.30) = 0.3286 \approx 0.33$$

$$\therefore \frac{x}{2\sqrt{Dt}} = 0.30 \quad \therefore x = 2 \times 0.30 \times \sqrt{3.091 \times 10^{-6} \times 10 \times 60} = 2.58 \times 10^{-2} \text{ cm} = \mathbf{258 \mu\text{m}}$$