

For an ideal gas,  $nN_A = PV/k_B T$  and so  $N = PV/k_B T$ . If  $T$  and  $V$  are held constant, we find

$$\frac{dN}{dt} = \frac{d}{dt} \left( \frac{PV}{k_B T} \right) = \frac{V}{k_B T} \frac{dP}{dt}$$

Use the first equation for rate of effusion to write

$$-\frac{V}{k_B T} \frac{dP}{dt} = \frac{PA}{(2\pi m k_B T)^{1/2}}$$

$$-\frac{dP}{dt} = \left( \frac{k_B T}{2\pi m} \right)^{1/2} \frac{A}{V} P = \alpha P$$

The solution to this equation is (as in the derivation of Equation 27.53)

$$P(t) = P(0)e^{-\alpha t}$$

27-53. How would you interpret the velocity distribution

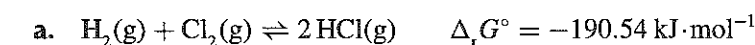
$$h(v_x, v_y, v_z) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[ -\frac{m}{2k_B T} \left\{ (v_x - a)^2 + (v_y - b)^2 + (v_z - c)^2 \right\} \right]$$

This is the velocity distribution relative to an overall translational motion of the system with velocity  $a\mathbf{i} + b\mathbf{j} + c\mathbf{k}$ .

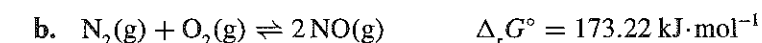
## Chemical Kinetics I: Rate Laws

## PROBLEMS AND SOLUTIONS

28-1. For each of the following chemical reactions, calculate the equilibrium extent of reaction at 298.15 K and one bar. (See Section 26-4.)



Initial amounts: one mole of  $\text{H}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$  and no  $\text{HCl}(\text{g})$ .



Initial amounts: one mole of  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$  and no  $\text{NO}(\text{g})$ .

- a. At equilibrium, there will be  $(1 - \xi_{\text{eq}})$  moles of  $\text{H}_2(\text{g})$  and  $\text{Cl}_2(\text{g})$ , and  $2\xi_{\text{eq}}$  moles of  $\text{HCl}(\text{g})$ . We can write the partial pressures of each species at equilibrium as

$$P_{\text{H}_2} = P_{\text{Cl}_2} = \frac{(1 - \xi_{\text{eq}})}{2} P \quad \text{and} \quad P_{\text{HCl}} = \frac{2\xi_{\text{eq}}}{2} P = \xi_{\text{eq}} P$$

where  $P$  is the total pressure. We can then write  $K_p$ , by definition, as

$$K_p = \frac{P_{\text{HCl}}^2}{P_{\text{H}_2} P_{\text{Cl}_2}} = \frac{(2\xi_{\text{eq}})^2}{(1 - \xi_{\text{eq}})^2}$$

Equating  $\ln K_p$  to  $-\Delta_r G^\circ / RT$  (Equation 26.11) allows us to write

$$\ln K_p = \frac{190.54 \text{ kJ} \cdot \text{mol}^{-1}}{(8.3145 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} = 76.862$$

$$K_p = 2.40 \times 10^{33}$$

$$\frac{(2\xi_{\text{eq}})^2}{(1 - \xi_{\text{eq}})^2} = 2.40 \times 10^{33}$$

Solving this equation for  $\xi_{\text{eq}}$  gives a value of  $\xi_{\text{eq}} = 1$  mol.

- b. At equilibrium, there will be  $(1 - \xi_{\text{eq}})$  moles of  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$ , and  $2\xi_{\text{eq}}$  moles of  $\text{NO}(\text{g})$ . We can write the partial pressures of each species at equilibrium as

$$P_{\text{N}_2} = P_{\text{O}_2} = \frac{(1 - \xi_{\text{eq}})}{2} P \quad \text{and} \quad P_{\text{NO}} = \frac{2\xi_{\text{eq}}}{2} P = \xi_{\text{eq}} P$$

where  $P$  is the total pressure. We can then write  $K_p$ , by definition, as

$$K_p = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = \frac{(2\xi_{\text{eq}})^2}{(1 - \xi_{\text{eq}})^2}$$

Equating  $\ln K_p$  to  $-\Delta_r G^\circ/RT$  (Equation 26.11) allows us to write

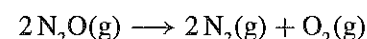
$$\ln K_p = \frac{-173.22 \text{ kJ} \cdot \text{mol}^{-1}}{(8.3145 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} = -69.87$$

$$K_p = 4.50 \times 10^{-31}$$

$$\frac{(2\xi_{\text{eq}})^2}{(1 - \xi_{\text{eq}})^2} = 4.50 \times 10^{-31}$$

Solving this equation for  $\xi_{\text{eq}}$  gives a value of  $\xi_{\text{eq}} = 3.3 \times 10^{-16} \text{ mol}$ .

**28-2.** Dinitrogen oxide,  $\text{N}_2\text{O}$ , decomposes according to the equation



Under certain conditions at 900 K, the rate of reaction is  $6.16 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ . Calculate the values of  $d[\text{N}_2\text{O}]/dt$ ,  $d[\text{N}_2]/dt$ , and  $d[\text{O}_2]/dt$ .

Using Equation 28-7, we see that for this reaction,

$$6.16 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1} = \frac{1}{2} \frac{d[\text{N}_2]}{dt} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

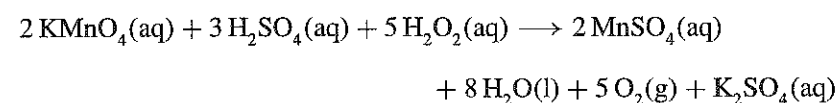
We find that  $d[\text{N}_2\text{O}]/dt = -1.23 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ ,  $d[\text{N}_2]/dt = 1.23 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ , and  $d[\text{O}_2]/dt = 6.16 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ .

**28-3.** Suppose the reaction in Problem 28-2 is carried out in a  $2.67 \text{ dm}^3$  container. Calculate the value of  $d\xi/dt$  corresponding to the rate of reaction of  $6.16 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ .

From Problem 28-2, we know that  $d[\text{O}_2]/dt = 6.16 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ . Using Equation 28.5 gives

$$\begin{aligned} \frac{1}{V} \frac{d\xi}{dt} &= \frac{d[\text{O}_2]}{dt} \\ \frac{d\xi}{dt} &= (6.16 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1})(2.67 \text{ dm}^3) = 1.64 \times 10^{-5} \text{ mol} \cdot \text{s}^{-1} \end{aligned}$$

**28-4.** The oxidation of hydrogen peroxide by permanganate occurs according to the equation

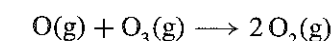


Define  $v$ , the rate of reaction, in terms of each of the reactants and products.

Using Equation 28.6, we write

$$\begin{aligned} v(t) &= -\frac{1}{2} \frac{d[\text{KMnO}_4]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2\text{SO}_4]}{dt} = -\frac{1}{5} \frac{d[\text{H}_2\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{MnSO}_4]}{dt} \\ &= \frac{1}{8} \frac{d[\text{H}_2\text{O}]}{dt} = \frac{1}{5} \frac{d[\text{O}_2]}{dt} = \frac{d[\text{K}_2\text{SO}_4]}{dt} \end{aligned}$$

**28-5.** The second-order rate constant for the reaction



is  $1.26 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ . Determine the value of the rate constant in units of  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

$$\left( \frac{1.26 \times 10^{-15} \text{ cm}^3}{\text{molecule} \cdot \text{s}} \right) \left( \frac{6.022 \times 10^{23} \text{ molecule}}{\text{mol}} \right) \left( \frac{1 \text{ dm}}{10 \text{ cm}} \right)^3 = 7.59 \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$$

**28-6.** The definition of the rate of reaction in terms of molar concentration (Equation 28.5) assumes that the volume remains constant during the course of the reaction. Derive an expression for the rate of reaction in terms of the molar concentration of a reactant A for the case in which the volume changes during the course of the reaction.

From the definition of molar concentration, we know that  $n_A = [\text{A}]V$ , and so

$$dn_A = Vd[\text{A}] + [\text{A}]dV \quad (1)$$

The rate of reaction is defined as

$$v = -\frac{1}{\nu_A V} \frac{dn_A}{dt}$$

and substituting  $dn_A$  from Equation 1 gives

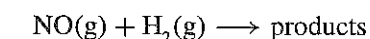
$$v = -\frac{1}{\nu_A} \frac{d[\text{A}]}{dt} - \frac{[\text{A}]}{\nu_A V} \frac{dV}{dt}$$

**28-7.** Derive the integrated rate law for a reaction that is zero order in reactant concentration.

The rate law for a zero-order reaction is  $v(t) = k$ , or  $-d[\text{A}]/dt = k$ . Integrating gives the integrated rate law

$$\begin{aligned} \int -d[\text{A}] &= \int k dt \\ [\text{A}] - [\text{A}]_0 &= -kt \end{aligned}$$

**28-8.** Determine the rate law for the reaction described by



from the initial rate data tabulated below.

$P_0(\text{H}_2)/\text{torr}$	$P_0(\text{NO})/\text{torr}$	$v_0/\text{torr}\cdot\text{s}^{-1}$
400	159	34
400	300	125
289	400	160
205	400	110
147	400	79

Calculate the rate constant for this reaction.

We do this problem in the same way as Example 28–2. The rate law has the form

$$v = k[\text{NO}]^{m_{\text{NO}}}[\text{H}_2]^{m_{\text{H}_2}}$$

To determine  $m_{\text{NO}}$ , we use Equation 28.19 and the first two entries in the data table to find

$$m_{\text{NO}} = \frac{\ln(34/125)}{\ln(159/300)} = 2.05 \approx 2$$

Likewise, using the third and fourth entries in the data table, we find that

$$m_{\text{H}_2} = \frac{\ln(160/110)}{\ln(289/205)} = 1.09 \approx 1$$

Assuming the orders are integer valued gives the rate law

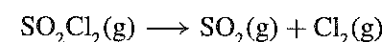
$$v = k[\text{NO}]^2[\text{H}_2]$$

We can substitute each set of data given in the table into the rate law to calculate the average rate constant. Below is a table of the rate constant found for each  $v_0$  in the table.

$v_0/\text{torr}\cdot\text{s}^{-1}$	34	125	160	110	79
$k/\text{torr}^{-2}\cdot\text{s}^{-1}$	$3.36 \times 10^{-6}$	$3.47 \times 10^{-6}$	$3.46 \times 10^{-6}$	$3.35 \times 10^{-6}$	$3.36 \times 10^{-6}$

The average value of  $k$  is  $3.40 \times 10^{-6} \text{ torr}^{-2}\cdot\text{s}^{-1}$ .

### 28–9. Sulfuryl chloride decomposes according to the equation



Determine the order of the reaction with respect to  $\text{SO}_2\text{Cl}_2(\text{g})$  from the following initial-rate data collected at 298.15 K.

$[\text{SO}_2\text{Cl}_2]_0/\text{mol}\cdot\text{dm}^{-3}$	0.10	0.37	0.76	1.22
$v_0/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$	$2.24 \times 10^{-6}$	$8.29 \times 10^{-6}$	$1.71 \times 10^{-5}$	$2.75 \times 10^{-5}$

Calculate the rate constant for this reaction at 298.15 K.

We do this problem in the same way as Example 28–2. The rate law has the form

$$v = k[\text{SO}_2\text{Cl}_2]^{m_{\text{SO}_2\text{Cl}_2}}$$

To determine  $m_{\text{SO}_2\text{Cl}_2}$ , we use Equation 28.19 and the second and third entries in the data table to find

$$m_{\text{SO}_2\text{Cl}_2} = \frac{\ln(8.29 \times 10^{-6}/1.71 \times 10^{-5})}{\ln(0.37/0.76)} = 1.01 \approx 1$$

Assuming the order is integer valued gives the rate law

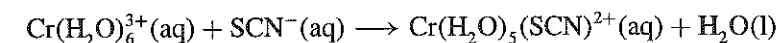
$$v = k[\text{SO}_2\text{Cl}_2]$$

We can substitute the data given in the table into the rate law to calculate the average rate constant. Below is a table of the rate constant found for each tabulated  $v_0$ .

$v_0/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$	$2.24 \times 10^{-6}$	$8.29 \times 10^{-6}$	$1.71 \times 10^{-5}$	$2.75 \times 10^{-5}$
$k/\text{s}^{-1}$	$2.24 \times 10^{-5}$	$2.24 \times 10^{-5}$	$2.25 \times 10^{-5}$	$2.25 \times 10^{-5}$

The average value of  $k$  is  $2.25 \times 10^{-5} \text{ s}^{-1}$ .

### 28–10. Consider the reaction described by



for which the following initial rate data were obtained at 298.15 K.

$[\text{Cr}(\text{H}_2\text{O})_6^{3+}]_0/\text{mol}\cdot\text{dm}^{-3}$	$[\text{SCN}^-]_0/\text{mol}\cdot\text{dm}^{-3}$	$v_0/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$
$1.21 \times 10^{-4}$	$1.05 \times 10^{-5}$	$2.11 \times 10^{-11}$
$1.46 \times 10^{-4}$	$2.28 \times 10^{-5}$	$5.53 \times 10^{-11}$
$1.66 \times 10^{-4}$	$1.02 \times 10^{-5}$	$2.82 \times 10^{-11}$
$1.83 \times 10^{-4}$	$3.11 \times 10^{-5}$	$9.44 \times 10^{-11}$

Determine the rate law for the reaction and the rate constant at 298.15 K. Assume the orders are integers.

The rate law has the form

$$v = k[\text{Cr}(\text{H}_2\text{O})_6^{3+}]^{m_{\text{Cr}(\text{H}_2\text{O})_6^{3+}}}[\text{SCN}^-]^{m_{\text{SCN}^-}}$$

The first and third entries in the data table are for an essentially constant concentration of  $[\text{SCN}^-]$ , so, proceeding as in Example 28–2,

$$m_{\text{Cr}(\text{H}_2\text{O})_6^{3+}} = \frac{\ln(2.82 \times 10^{-11}/2.11 \times 10^{-11})}{\ln(1.66 \times 10^{-4}/1.21 \times 10^{-4})} = 0.917 \approx 1$$

Using this result and the first two entries of the data table, we have the rate equations

$$2.11 \times 10^{-11} \text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1} = k(1.21 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3})(1.05 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3})^{m_{\text{SCN}^-}}$$

$$5.53 \times 10^{-11} \text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1} = k(1.46 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3})(2.28 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3})^{m_{\text{SCN}^-}}$$

Taking the ratio of these two equations gives

$$0.460 = (0.460)^{m_{\text{SCN}^-}}$$

from which we find  $m_{\text{SCN}^-} = 1$ . The rate law is first order in each reagent and second order overall:

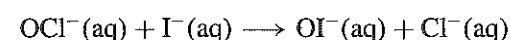
$$v = k[\text{Cr}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]$$

We can substitute the data given in the table into the rate law to calculate the average rate constant. The four sets of data give rate constants of

$v_0/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$	$2.11 \times 10^{-11}$	$5.53 \times 10^{-11}$	$2.82 \times 10^{-11}$	$9.44 \times 10^{-11}$
$k/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	$1.66 \times 10^{-2}$	$1.66 \times 10^{-2}$	$1.67 \times 10^{-2}$	$1.66 \times 10^{-2}$

and the average value of  $k$  is  $1.66 \times 10^{-2} \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ .

### 28-11. Consider the base-catalyzed reaction



Use the following initial-rate data to determine the rate law and the corresponding rate constant for the reaction.

$[\text{OCl}^-]/\text{mol}\cdot\text{dm}^{-3}$	$[\text{I}^-]/\text{mol}\cdot\text{dm}^{-3}$	$[\text{OH}^-]/\text{mol}\cdot\text{dm}^{-3}$	$v_0/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$
$1.62 \times 10^{-3}$	$1.62 \times 10^{-3}$	0.52	$3.06 \times 10^{-4}$
$1.62 \times 10^{-3}$	$2.88 \times 10^{-3}$	0.52	$5.44 \times 10^{-4}$
$2.71 \times 10^{-3}$	$1.62 \times 10^{-3}$	0.84	$3.16 \times 10^{-4}$
$1.62 \times 10^{-3}$	$2.88 \times 10^{-3}$	0.91	$3.11 \times 10^{-4}$

Because the reaction is base-catalyzed, the rate will depend on the basicity of the solution, or on the concentration of  $\text{OH}^-$  present. Therefore, the rate law has the form

$$v = k[\text{OCl}^-]^{m_{\text{OCl}^-}}[\text{I}^-]^{m_{\text{I}^-}}[\text{OH}^-]^{m_{\text{OH}^-}}$$

The first two entries in the data table hold  $[\text{OCl}^-]$  and  $[\text{OH}^-]$  constant, so we write (as in Example 28-2)

$$m_{\text{I}^-} = \frac{\ln(3.06 \times 10^{-4}/5.44 \times 10^{-4})}{\ln(1.62 \times 10^{-3}/2.88 \times 10^{-3})} = 1$$

The second and fourth entries in the data table hold  $[\text{OCl}^-]$  and  $[\text{I}^-]$  constant, so we write

$$m_{\text{OH}^-} = \frac{\ln(5.44 \times 10^{-4}/3.11 \times 10^{-4})}{\ln(0.52/0.91)} = -0.9991 \approx -1$$

Using these results and the first and third entries of the data table, we have the rate equations

$$3.06 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1} = k \frac{(1.62 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3})^{m_{\text{OCl}^-}}(1.62 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3})}{0.52 \text{ mol}\cdot\text{dm}^{-3}}$$

$$3.16 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1} = k \frac{(2.71 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3})^{m_{\text{OCl}^-}}(1.62 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3})}{0.84 \text{ mol}\cdot\text{dm}^{-3}}$$

Taking the ratio of these two equations gives

$$0.599 = (0.598)^{m_{\text{OCl}^-}}$$

from which we find  $m_{\text{OCl}^-} = 1$ . The rate law is therefore

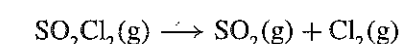
$$v = k \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$$

We can substitute the data given in the table into the rate law to calculate the average rate constant. The four sets of data give rate constants of

$v_0/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$	$3.06 \times 10^{-4}$	$5.44 \times 10^{-4}$	$3.16 \times 10^{-4}$	$3.11 \times 10^{-4}$
$k/\text{s}^{-1}$	60.6	60.6	60.5	60.7

and the average value of  $k$  is  $60.6 \text{ s}^{-1}$ .

### 28-12. The reaction



is first order and has a rate constant of  $2.24 \times 10^{-5} \text{ s}^{-1}$  at  $320^\circ\text{C}$ . Calculate the half-life of the reaction. What fraction of a sample of  $\text{SO}_2\text{Cl}_2(\text{g})$  remains after being heated for 5.00 hours at  $320^\circ\text{C}$ ? How long will a sample of  $\text{SO}_2\text{Cl}_2(\text{g})$  need to be maintained at  $320^\circ\text{C}$  to decompose 92.0% of the initial amount present?

The integrated rate law for a first order reaction is

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -kt \quad (28.22)$$

At  $t = t_{1/2}$ ,  $[\text{SO}_2\text{Cl}_2] = \frac{1}{2}[\text{SO}_2\text{Cl}_2]_0$ , and substituting into Equation 28.22 gives

$$\ln \frac{1}{2} = -(2.24 \times 10^{-5} \text{ s}^{-1})t_{1/2}$$

$$3.09 \times 10^4 \text{ s} = t_{1/2}$$

After being heated for 5.00 hours at  $320^\circ\text{C}$ , the amount of  $\text{SO}_2\text{Cl}_2$  present can be found by solving the equation

$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -(2.24 \times 10^{-5} \text{ s}^{-1})(5.00 \text{ hr})(3600 \text{ s}\cdot\text{hr}^{-1})$$

$$[\text{SO}_2\text{Cl}_2] = 0.668[\text{SO}_2\text{Cl}_2]_0$$

In other words, 68.8% of the sample will remain. The time it takes to decompose 92.0% of  $\text{SO}_2\text{Cl}_2$  can be found by solving

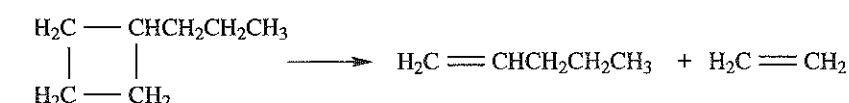
$$\ln \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = -(2.24 \times 10^{-5} \text{ s}^{-1})t$$

$$\ln(1 - 0.920) = -(2.24 \times 10^{-5} \text{ s}^{-1})t$$

$$1.13 \times 10^5 \text{ s} = t$$

It takes 31.3 hours to decompose 92.0% of the initial amount of  $\text{SO}_2\text{Cl}_2$  present.

### 28-13. The half-life for the following gas-phase decomposition reaction



is found to be independent of the initial concentration of the reactant. Determine the rate law and integrated rate law for this reaction.

This is a first-order reaction, because the half-life is independent of the initial reactant concentration. The rate law and integrated rate law for the reaction are  $v = k[A]$  and  $[A] = [A]_0 e^{-kt}$ , respectively, where A represents the reactant.

- 28-14.** Hydrogen peroxide,  $\text{H}_2\text{O}_2$ , decomposes in water by a first-order kinetic process. A  $0.156\text{-mol}\cdot\text{dm}^{-3}$  solution of  $\text{H}_2\text{O}_2$  in water has an initial rate of  $1.14 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$ . Calculate the rate constant for the decomposition reaction and the half-life of the decomposition reaction.

We can find the rate constant by substituting into the first-order rate law (Equation 28.21):

$$v_0 = k[\text{H}_2\text{O}_2]_0$$

$$k = \frac{1.14 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}}{0.156\text{ mol}\cdot\text{dm}^{-3}} = 7.31 \times 10^{-5}\text{ s}^{-1}$$

For a first-order reaction, we can use Equation 28.25 to determine the half-life of the reaction:

$$t_{1/2} = \frac{\ln 2}{k} = 9.48 \times 10^3\text{ s} = 2.63\text{ hr}$$

- 28-15.** A first-order reaction is 24.0% complete in 19.7 minutes. How long will the reaction take to be 85.5% complete? Calculate the rate constant for the reaction.

To find the rate constant of the reaction, we can write (from Equation 28.22)

$$\ln \frac{[A]}{[A]_0} = -k(19.7\text{ min})$$

$$\ln(1 - 0.24) = -k(19.7\text{ min})$$

$$1.39 \times 10^{-2}\text{ min}^{-1} = k$$

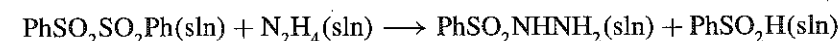
To find the time it takes for the reaction to be 85.5% complete, we solve the equation

$$\ln \frac{[A]}{[A]_0} = -(1.39 \times 10^{-2}\text{ min}^{-1})t$$

$$\ln(1 - 0.855) = -(1.39 \times 10^{-2}\text{ min}^{-1})t$$

$$139\text{ min} = t$$

- 28-16.** The nucleophilic substitution reaction



was studied in cyclohexane solution at 300 K. The rate law was found to be first order in  $\text{PhSO}_2\text{SO}_2\text{Ph}$ . For an initial concentration of  $[\text{PhSO}_2\text{SO}_2\text{Ph}]_0 = 3.15 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}$ , the following rate data were observed. Determine the rate law and the rate constant for this reaction.

$[\text{N}_2\text{H}_4]_0/10^{-2}\text{ mol}\cdot\text{dm}^{-3}$	0.5	1.0	2.4	5.6
$v/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$	0.085	0.17	0.41	0.95

We know that the rate law is first order in  $\text{PhSO}_2\text{SO}_2\text{Ph}$ , so we can write the rate law as

$$v = k[\text{PhSO}_2\text{SO}_2\text{Ph}][\text{N}_2\text{H}_4]^{m_{\text{N}_2\text{H}_4}}$$

To determine  $m_{\text{N}_2\text{H}_4}$ , we use Equation 28.19 and the first two sets of data in the table to find

$$m_{\text{N}_2\text{H}_4} = \frac{\ln(0.085/0.17)}{\ln(0.5/1.0)} = 1$$

This gives the rate law

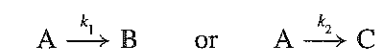
$$v = k[\text{PhSO}_2\text{SO}_2\text{Ph}][\text{N}_2\text{H}_4]$$

We can substitute each set of data given in the table into the rate law to calculate the average rate constant:

$v/\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$	0.085	0.17	0.41	0.95
$k/\text{dm}^3\cdot\text{s}^{-1}\cdot\text{mol}^{-1}$	$5.4 \times 10^5$	$5.4 \times 10^5$	$5.4 \times 10^5$	$5.4 \times 10^5$

The average value of  $k$  is  $5.4 \times 10^5\text{ dm}^3\cdot\text{s}^{-1}\cdot\text{mol}^{-1}$ .

- 28-17.** Show that if A reacts to form either B or C according to



then

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

Now show that  $t_{1/2}$ , the half-life of A, is given by

$$t_{1/2} = \frac{0.693}{k_1 + k_2}$$

Show that  $[\text{B}]/[\text{C}] = k_1/k_2$  for all times  $t$ . For the set of initial conditions  $[A] = [A]_0$ ,  $[\text{B}]_0 = [\text{C}]_0 = 0$ , and  $k_2 = 4k_1$ , plot  $[A]$ ,  $[\text{B}]$ , and  $[\text{C}]$  as a function of time on the same graph.

If A simultaneously reacts to form B and C, we can write

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$\frac{d[A]}{[A]} = -(k_1 + k_2)dt$$

$$\ln \frac{[A]}{[A]_0} = -(k_1 + k_2)t$$

$$[A] = [A]_0 e^{-(k_1+k_2)t}$$

Now, at the half life of the reaction ( $t = t_{1/2}$ ), we have

$$\ln \frac{1}{2} = -(k_1 + k_2)t_{1/2}$$

$$\frac{0.693}{k_1 + k_2} = t_{1/2}$$



We can write

$$\frac{d[B]}{dt} = k_1[A] = k_1[A]_0 e^{-(k_1+k_2)t}$$

and

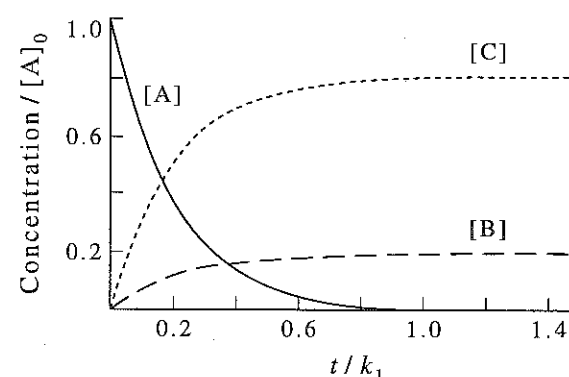
$$\frac{d[C]}{dt} = k_2[A] = k_2[A]_0 e^{-(k_1+k_2)t}$$

Because  $[B]_0 = [C]_0 = 0$ , we integrate the above expressions to get

$$[B] = \frac{k_1[A]_0}{k_1 + k_2} [1 - e^{-(k_1+k_2)t}]$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2} [1 - e^{-(k_1+k_2)t}]$$

from which we see that  $[B]/[C] = k_1/k_2$  for all times  $t$ . The plot below shows  $[A]$ ,  $[B]$ , and  $[C]$  as functions of time.



The following six problems deal with the decay of radioactive isotopes, which is a first-order process. Therefore, if  $N(t)$  is the number of a radioactive isotope at time  $t$ , then  $N(t) = N(0)e^{-kt}$ . In dealing with radioactive decay, the half-life,  $t_{1/2} = 0.693/k$ , is almost exclusively used to describe the rate of decay (the kinetics of decay).

- 28-18.** You order a sample of  $\text{Na}_3\text{PO}_4$  containing the radioisotope phosphorus-32 ( $t_{1/2} = 14.3$  days). If the shipment is delayed in transit for two weeks, how much of the original activity will remain when you receive the sample?

The rate constant for this reaction is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.3 \text{ days}} = 4.85 \times 10^{-2} \text{ days}^{-1}$$

Then

$$\begin{aligned} N(t) &= N(0)e^{-kt} \\ \frac{N(t)}{N(0)} &= e^{-(4.85 \times 10^{-2} \text{ days}^{-1})(14 \text{ days})} = 0.507 \end{aligned}$$

50.7% of the original activity will remain when you receive the sample.

- 28-19.** Copper-64 ( $t_{1/2} = 12.8$  h) is used in brain scans for tumors and in studies of Wilson's disease (a genetic disorder characterized by the inability to metabolize copper). Calculate the number of days required for an administered dose of copper-64 to drop to 0.10% of the initial value injected. Assume no loss of copper-64 except by radioactive decay.

To find the time required, we solve the equation

$$\frac{N(t)}{N(0)} = 0.0010 = e^{-0.693t/12.8 \text{ h}}$$

to find  $t = 128 \text{ hour} = 5.32 \text{ days}$ .

- 28-20.** Sulfur-38 can be incorporated into proteins to follow certain aspects of protein metabolism. If a protein sample initially has an activity of  $10\,000 \text{ disintegrations} \cdot \text{min}^{-1}$ , calculate the activity 6.00 h later. The half-life of sulfur-38 is 2.84 h. *Hint:* Use the fact that the rate of decay is proportional to  $N(t)$  for a first-order process.

Because the rate of decay is proportional to  $N(t)$ , we can write

$$\begin{aligned} \frac{N(6.00 \text{ h})}{N(0 \text{ h})} &= \frac{\text{rate of decay (6.00 h)}}{\text{rate of decay (0 h)}} = e^{-(0.693)(6.00 \text{ h})/2.84 \text{ h}} \\ \text{decay rate (6.00 h)} &= (10\,000 \text{ disintegrations} \cdot \text{min}^{-1})(0.231) \\ &= 2310 \text{ disintegrations} \cdot \text{min}^{-1} \end{aligned}$$

- 28-21.** The radioisotope phosphorus-32 can be incorporated into nucleic acids to follow certain aspects of their metabolism. If a nucleic acid sample initially has an activity of  $40\,000 \text{ disintegrations} \cdot \text{min}^{-1}$ , calculate the activity 220 h later. The half-life of phosphorus-32 is 14.28 d. *Hint:* Use the fact that the rate of decay is proportional to  $N(t)$  for a first-order process.

As in Problem 28-20, we can write

$$\begin{aligned} \frac{\text{rate of decay (220 h)}}{\text{rate of decay (0 h)}} &= e^{-(0.693)(220 \text{ h})/(342.72 \text{ h})} \\ \text{decay rate (220 h)} &= (40\,000 \text{ disintegrations} \cdot \text{min}^{-1})(0.64) \\ &= 26\,000 \text{ disintegrations} \cdot \text{min}^{-1} \end{aligned}$$

- 28-22.** Uranium-238 decays to lead-206 with a half-life of  $4.51 \times 10^9$  y. A sample of ocean sediment is found to contain 1.50 mg of uranium-238 and 0.460 mg of lead-206. Estimate the age of the sediment assuming that lead-206 is formed only by the decay of uranium and that lead-206 does not itself decay.

The amount of U-238 which must have decayed to form 0.460 mg of Pb-206 is

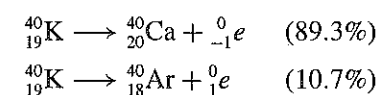
$$(0.460 \text{ mg Pb}) \left( \frac{1 \text{ mol Pb}}{206 \text{ g Pb}} \right) \left( \frac{1 \text{ mol U}}{1 \text{ mol Pb}} \right) \left( \frac{238 \text{ g U}}{1 \text{ mol U}} \right) = 0.531 \text{ mg U}$$

At  $t = 0$ , therefore, there are  $1.50 \text{ mg} + 0.531 \text{ mg} = 2.03 \text{ mg}$  of uranium in the sediment. Then

$$\ln \frac{1.50 \text{ mg}}{2.03 \text{ mg}} = -\frac{\ln 2}{4.51 \times 10^9 \text{ y}} t$$

$$1.97 \times 10^9 \text{ y} = t$$

**28-23.** Potassium-argon dating is used in geology and archeology to date sedimentary rocks. Potassium-40 decays by two different paths



The overall half-life for the decay of potassium-40 is  $1.3 \times 10^9 \text{ y}$ . Estimate the age of sedimentary rocks with an argon-40 to potassium-40 ratio of 0.0102. (See Problem 28-17.)

From Problem 28-17, we have the expressions

$$[\text{K}] = [\text{K}]_0 e^{-(k_1+k_2)t} \quad \text{and} \quad t_{1/2} = \frac{\ln 2}{k_1 + k_2}$$

We can substitute the overall half-life of potassium-40 into the second equation to find  $k_1 + k_2$ :

$$k_1 + k_2 = \frac{\ln 2}{t_{1/2}} = 5.33 \times 10^{-10} \text{ y}^{-1}$$

For every mole of potassium which decays, 0.107 moles of argon are formed. Assuming that the only source of argon is potassium decay, we can find the ratio of potassium present at time  $t$  to potassium originally present:

$$\left( \frac{0.0102 \text{ mol Ar at } t}{1 \text{ mol K at } t} \right) \left( \frac{1 \text{ mol K decayed}}{0.107 \text{ mol Ar at } t} \right) = \frac{0.0953 \text{ mol K decayed}}{1 \text{ mol K at } t}$$

There were 1.0953 mol of potassium originally present for every mole present at time  $t$ . Now substitute this value into Equation 1:

$$[\text{K}] = [\text{K}]_0 e^{-(5.33 \times 10^{-10} \text{ y}^{-1})t}$$

$$\ln \frac{1}{1.0953} = -(5.33 \times 10^{-10} \text{ y}^{-1})t$$

$$1.71 \times 10^8 \text{ y} = t$$

**28-24.** In this problem, we will derive Equation 28.32 from the rate law (Equation 28.31)

$$-\frac{d[\text{A}]}{dt} = k[\text{A}][\text{B}] \quad (1)$$

Use the reaction stoichiometry of Equation 28.30 to show that  $[\text{B}] = [\text{B}]_0 - [\text{A}]_0 + [\text{A}]$ . Use this result to show that Equation 1 can be written as

$$-\frac{d[\text{A}]}{dt} = k[\text{A}][[\text{B}]_0 - [\text{A}]_0 + [\text{A}]]$$

Now separate the variables and then integrate the resulting equation subject to its initial conditions to obtain the desired result, Equation 28.32:

$$kt = \frac{1}{[\text{A}]_0 - [\text{B}]_0} \ln \frac{[\text{A}][\text{B}]_0}{[\text{B}][\text{A}]_0}$$

The amount of  $[\text{B}]$  present is equal to the amount of B reacted subtracted from  $[\text{B}]_0$ . Because one mole of A reacts with one mole of B, we can express the amount of B reacted as  $[\text{A}]_0 - [\text{A}]$ , so  $[\text{B}] = [\text{B}]_0 - ([\text{A}]_0 - [\text{A}]) = [\text{B}]_0 - [\text{A}]_0 + [\text{A}]$ . Substituting into Equation 1 gives

$$-\frac{d[\text{A}]}{dt} = k[\text{A}][[\text{B}]_0 - [\text{A}]_0 + [\text{A}]]$$

$$-\frac{d[\text{A}]}{[\text{A}][[\text{B}]_0 - [\text{A}]_0 + [\text{A}]]} = kdt$$

$$-\frac{1}{[\text{B}]_0 - [\text{A}]_0} \ln \frac{[\text{A}]}{[\text{B}]_0 - [\text{A}]_0 + [\text{A}]} \Big|_{[\text{A}]_0}^{[\text{A}]} = kt$$

$$\frac{1}{[\text{A}]_0 - [\text{B}]_0} \ln \frac{[\text{A}][\text{B}]_0}{[\text{A}]_0[\text{B}]} = kt$$

**28-25.** Equation 28.32 is indeterminate if  $[\text{A}]_0 = [\text{B}]_0$ . Use L'Hopital's rule to show that Equation 28.32 reduces to Equation 28.33 when  $[\text{A}]_0 = [\text{B}]_0$ . (Hint: Let  $[\text{A}] = [\text{B}] + x$  and  $[\text{A}]_0 = [\text{B}]_0 + x$ .)

We begin with Equation 28.32,

$$kt = \frac{1}{[\text{A}]_0 - [\text{B}]_0} \ln \frac{[\text{A}][\text{B}]_0}{[\text{B}][\text{A}]_0}$$

Let  $[\text{A}] = [\text{B}] + x$  and  $[\text{A}]_0 = [\text{B}]_0 + x$ . Then we can write Equation 28.32 as

$$kt = \frac{1}{[\text{B}]_0 + x - [\text{B}]_0} \ln \frac{([\text{B}] + x)[\text{B}]_0}{[\text{B}][[\text{B}]_0 + x]} = \frac{1}{x} \ln \frac{([\text{B}] + x)[\text{B}]_0}{[\text{B}][[\text{B}]_0 + x]}$$

Now, as  $x \rightarrow 0$ ,

$$\lim_{x \rightarrow 0} kt = \lim_{x \rightarrow 0} \frac{1}{x} \ln \frac{([\text{B}] + x)[\text{B}]_0}{[\text{B}][[\text{B}]_0 + x]}$$

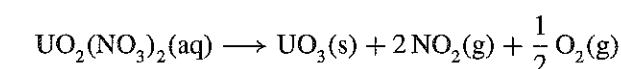
$$= \lim_{x \rightarrow 0} \frac{\ln([\text{B}] + x) - \ln[\text{B}] + \ln[\text{B}]_0 - \ln([\text{B}]_0 + x)}{x}$$

This fraction is indeterminate, so we use L'Hopital's rule to write

$$\lim_{x \rightarrow 0} kt = \lim_{x \rightarrow 0} \left( \frac{1}{[\text{B}] + x} - \frac{1}{[\text{B}]_0 + x} \right)$$

$$= \frac{1}{[\text{B}]} - \frac{1}{[\text{B}]_0}$$

**28-26.** Uranyl nitrate decomposes according to

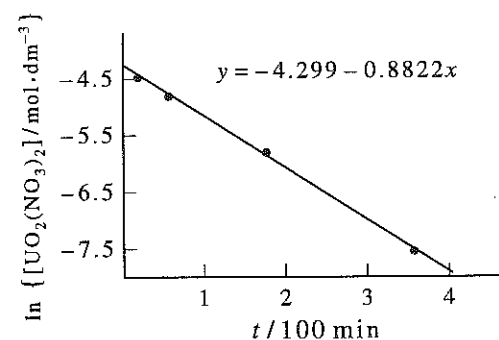


The rate law for this reaction is first order in the concentration of uranyl nitrate. The following data were recorded for the reaction at 25.0°C.

$t/\text{min}$	0	20.0	60.0	180.0	360.0
$[\text{UO}_2(\text{NO}_3)_2]/\text{mol}\cdot\text{dm}^{-3}$	0.01413	0.01096	0.00758	0.00302	0.00055

Calculate the rate constant for this reaction at 25.0°C.

Because the reaction is first-order, a plot of  $\ln[\text{UO}_2(\text{NO}_3)_2]$  versus time should give a straight line of slope  $-k$ .



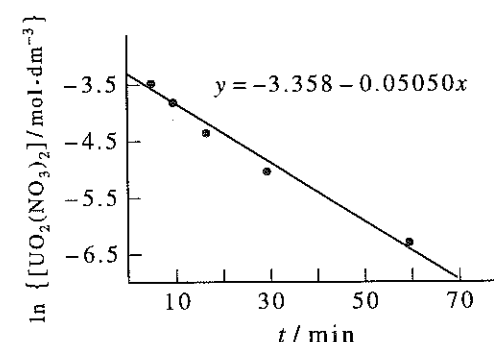
The slope of the best-fit line is  $-8.82 \times 10^{-3} \text{ min}^{-1}$ , so  $k = 8.82 \times 10^{-3} \text{ min}^{-1}$ .

28–27. The data for the decomposition of uranyl nitrate (Problem 28–26) at 350°C are tabulated below

$t/\text{min}$	0	6.0	10.0	17.0	30.0	60.0
$[\text{UO}_2(\text{NO}_3)_2]/\text{mol}\cdot\text{dm}^{-3}$	0.03802	0.02951	0.02089	0.01259	0.00631	0.00191

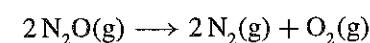
Calculate the rate constant for this reaction at 350°C.

Again, because the reaction is first-order, a plot of  $\ln[\text{UO}_2(\text{NO}_3)_2]$  versus time should give a straight line of slope  $-k$ .



The slope of the best fit line is  $-0.0505 \text{ min}^{-1}$ , so  $k = 5.05 \times 10^{-2} \text{ min}^{-1}$ .

28–28. The following data are obtained for the reaction

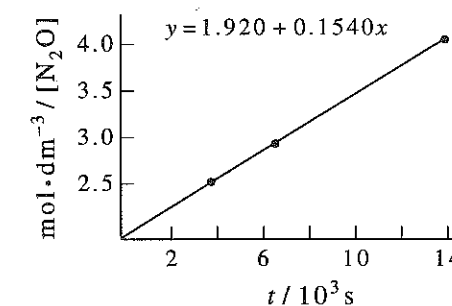


at 900 K.

$t/\text{s}$	0	3146	6494	13 933
$[\text{N}_2\text{O}]/\text{mol}\cdot\text{dm}^{-3}$	0.521	0.416	0.343	0.246

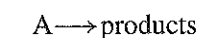
The rate law for this reaction is second order in  $\text{N}_2\text{O}$  concentration. Calculate the rate constant for this decomposition reaction.

Because the reaction is second-order in  $\text{N}_2\text{O}$ , a plot of  $1/[\text{N}_2\text{O}]$  versus time should give a straight line of slope  $k$ .



The slope of the best-fit line is  $1.54 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$ , so this is the value of  $k$  for the decomposition reaction.

28–29. Consider a chemical reaction



that obeys the rate law

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^n$$

where  $n$ , the reaction order, can be any number except  $n = 1$ . Separate the concentration and time variables and then integrate the resulting expression assuming the concentration of A is  $[\text{A}]_0$  at time  $t = 0$  and is  $[\text{A}]$  at time  $t$  to show that

$$kt = \frac{1}{n-1} \left( \frac{1}{[\text{A}]^{n-1}} - \frac{1}{[\text{A}]_0^{n-1}} \right) \quad n \neq 1 \quad (1)$$

Use Equation 1 to show that the half-life of a reaction of order  $n$  is

$$kt_{1/2} = \frac{1}{n-1} \frac{2^{n-1} - 1}{[\text{A}]_0^{n-1}} \quad n \neq 1 \quad (2)$$

Show that this result reduces to Equation 28.29 when  $n = 2$ .

Separating the variables in the rate law and integrating gives

$$\begin{aligned} -\frac{d[\text{A}]}{[\text{A}]^n} &= kdt \\ \frac{1}{n-1} \frac{1}{[\text{A}]^{n-1}} \Big|_{[\text{A}]_0}^{[\text{A}]} &= kt \\ \frac{1}{n-1} \left( \frac{1}{[\text{A}]^{n-1}} - \frac{1}{[\text{A}]_0^{n-1}} \right) &= kt \end{aligned} \quad (1)$$



where  $n \neq 1$  (if  $n = 1$ , the integration is incorrect). At  $t = t_{1/2}$ ,  $[A] = [A]_0/2$ , so Equation 1 becomes

$$kt_{1/2} = \frac{1}{n-1} \left[ \frac{1}{(\frac{1}{2}[A])^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] \\ = \frac{1}{n-1} \frac{2^{n-1} - 1}{[A]_0^{n-1}} \quad (2)$$

where, again,  $n \neq 1$ . When  $n = 2$ , this result becomes

$$kt_{1/2} = \frac{1}{[A]_0} \quad (28.29)$$

**28–30.** Show that Equation 1 of Problem 28–29 can be written in the form

$$\frac{\left(\frac{[A]_0}{[A]}\right)^x - 1}{x} = k[A]_0^x t$$

where  $x = n - 1$ . Now use L'Hopital's rule to show that

$$\ln \frac{[A]}{[A]_0} = -kt$$

for  $n = 1$ . (Remember that  $da^x/dx = a^x \ln a$ .)

Starting with Equation 1 of Problem 28–29, we can write

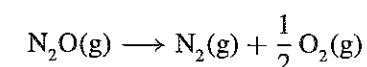
$$kt = \frac{1}{n-1} \left( \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) \\ (n-1)kt = \frac{[A]_0^{n-1} - [A]^{n-1}}{[A]^{n-1}[A]_0^{n-1}} \\ (n-1)k[A]_0^{n-1}t = \frac{[A]_0^{n-1}}{[A]^{n-1}} - 1$$

If we let  $x = n - 1$ , then we have the desired result. We can now use L'Hopital's rule to find the value of  $kt$  as  $x \rightarrow 0$  ( $n \rightarrow 1$ ):

$$\lim_{x \rightarrow 0} kt = \lim_{x \rightarrow 0} \frac{\left(\frac{1}{[A]}\right)^x - \left(\frac{1}{[A]_0}\right)^x}{x} \\ \lim_{x \rightarrow 0} kt = \lim_{x \rightarrow 0} \left[ \left(\frac{1}{[A]}\right)^x \ln \frac{1}{[A]} - \left(\frac{1}{[A]_0}\right)^x \ln \frac{1}{[A]_0} \right] = \ln \frac{[A]_0}{[A]} \\ -kt = \ln \frac{[A]}{[A]_0}$$

as  $n \rightarrow 1$ .

**28–31.** The following data were obtained for the reaction



$[\text{N}_2\text{O}]_0/\text{mol}\cdot\text{dm}^{-3}$	$1.674 \times 10^{-3}$	$4.458 \times 10^{-3}$	$9.300 \times 10^{-3}$	$1.155 \times 10^{-2}$
$t_{1/2}/\text{s}$	1200	470	230	190

Assume the rate law for this reaction is

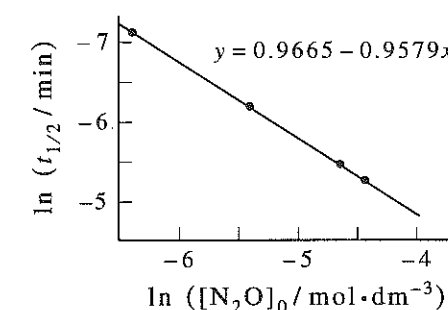
$$-\frac{d[\text{N}_2\text{O}]}{dt} = k[\text{N}_2\text{O}]^n$$

and use Equation 2 of Problem 28–29 to determine the reaction order of  $\text{N}_2\text{O}$  by plotting  $\ln t_{1/2}$  against  $\ln[A]_0$ . Calculate the rate constant for this decomposition reaction.

We can take the natural logarithm of both sides of Equation 2 of Problem 28–29 to write the equation as

$$\ln k + \ln t_{1/2} = (1-n) \ln[A]_0 + \ln \left[ \frac{1}{n-1} (2^{n-1} - 1) \right]$$

The slope of a plot of  $\ln t_{1/2}$  versus  $\ln[A]_0$  will be  $(1-n)$ . The data provided are plotted in this form in the following graph.



The slope of the plot of  $\ln t_{1/2}$  versus  $\ln[\text{N}_2\text{O}]_0$  is  $-1$ , so  $n = 2$  and the reaction is second-order in  $[\text{N}_2\text{O}]$ . We use Equation 28.29 and the data provided to find the value of the rate constant:

$[\text{N}_2\text{O}]_0/\text{mol}\cdot\text{dm}^{-3}$	$1.674 \times 10^{-3}$	$4.458 \times 10^{-3}$	$9.300 \times 10^{-3}$	$1.155 \times 10^{-2}$
$k/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	0.50	0.48	0.47	0.46

The average value of the rate constant is  $k = 0.47 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ .

**28–32.** We will derive Equation 28.39 from Equation 28.38 in this problem. Rearrange Equation 28.38 to become

$$\frac{d[A]}{(k_1 + k_{-1})[A] - k_{-1}[A]_0} = -dt$$

and integrate to obtain

$$\ln\{(k_1 + k_{-1})[A] - k_{-1}[A]_0\} = -(k_1 + k_{-1})t + \text{constant}$$

or

$$(k_1 + k_{-1})[A] - k_{-1}[A]_0 = ce^{-(k_1 + k_{-1})t}$$

where  $c$  is a constant. Show that  $c = k_1[A]_0$  and that

$$(k_1 + k_{-1})[A] - k_{-1}[A]_0 = k_1[A]_0 e^{-(k_1 + k_{-1})t} \quad (1)$$

Now let  $t \rightarrow \infty$  and show that

$$[A]_0 = \frac{(k_1 + k_{-1})[A]_{\text{eq}}}{k_{-1}}$$

and

$$[A]_0 - [A]_{\text{eq}} = \frac{k_1[A]_{\text{eq}}}{k_{-1}} = \frac{k_1[A]_0}{k_1 + k_{-1}}$$

Use these results in Equation 1 to obtain Equation 28.39.

We begin by separating the variables in Equation 28.38:

$$\begin{aligned} -\frac{d[A]}{dt} &= (k_1 + k_{-1})[A] - k_{-1}[A]_0 \\ \frac{d[A]}{(k_1 + k_{-1})[A] - k_{-1}[A]_0} &= -dt \end{aligned}$$

We then integrate to find

$$\begin{aligned} \int \frac{d[A]}{(k_1 + k_{-1})[A] - k_{-1}[A]_0} &= -\int dt \\ \frac{\ln\{(k_1 + k_{-1})[A] - k_{-1}[A]_0\}}{k_1 + k_{-1}} &= -t + \text{constant} \\ \ln\{(k_1 + k_{-1})[A] - k_{-1}[A]_0\} &= -(k_1 + k_{-1})t + \text{constant} \\ (k_1 + k_{-1})[A] - k_{-1}[A]_0 &= ce^{-(k_1 + k_{-1})t} \end{aligned} \quad (a)$$

where  $c$  is a constant. At  $t = 0$ ,  $[A] = [A]_0$ , so Equation a becomes

$$\begin{aligned} (k_1 + k_{-1} - k_{-1})[A]_0 &= c \\ k_1[A]_0 &= c \end{aligned}$$

Substituting this result back into Equation a gives Equation 1:

$$(k_1 + k_{-1})[A] - k_{-1}[A]_0 = k_1[A]_0 e^{-(k_1 + k_{-1})t} \quad (1)$$

Now let  $t \rightarrow \infty$ , in which case  $[A] \rightarrow [A]_{\text{eq}}$ . The exponential term in Equation 1 then goes to zero, and so

$$\begin{aligned} (k_1 + k_{-1})[A]_{\text{eq}} - k_{-1}[A]_0 &= 0 \\ [A]_0 &= \frac{(k_1 + k_{-1})[A]_{\text{eq}}}{k_{-1}} \end{aligned}$$

Subtracting  $[A]_{\text{eq}}$  from both sides gives

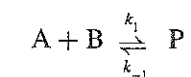
$$[A]_0 - [A]_{\text{eq}} = \frac{(k_1 + k_{-1} - k_{-1})[A]_{\text{eq}}}{k_{-1}} = \frac{k_1[A]_{\text{eq}}}{k_{-1}} = \frac{k_1[A]_0}{k_1 + k_{-1}}$$

Substituting into Equation 1 gives

$$\begin{aligned} (k_1 + k_{-1})[A] - k_{-1}[A]_0 &= k_1[A]_0 e^{-(k_1 + k_{-1})t} \\ [A] &= \frac{k_{-1}[A]_0}{k_1 + k_{-1}} + \frac{k_1[A]_0}{k_1 + k_{-1}} e^{-(k_1 + k_{-1})t} \\ [A] &= [A]_{\text{eq}} + ([A]_0 - [A]_{\text{eq}})e^{-(k_1 + k_{-1})t} \end{aligned}$$

which is Equation 28.39.

28–33. Consider the general chemical reaction



If we assume that both the forward and reverse reactions are first order in their respective reactants, the rate law is given by (Equation 28.52)

$$\frac{d[P]}{dt} = k_1[A][B] - k_{-1}[P] \quad (1)$$

Now consider the response of this chemical reaction to a temperature jump. Let  $[A] = [A]_{2,\text{eq}} + \Delta[A]$ ,  $[B] = [B]_{2,\text{eq}} + \Delta[B]$ , and  $[P] = [P]_{2,\text{eq}} + \Delta[P]$ , where the subscript “2,eq” refers to the new equilibrium state. Now use the fact that  $\Delta[A] = \Delta[B] = -\Delta[P]$  to show that Equation 1 becomes

$$\begin{aligned} \frac{d\Delta[P]}{dt} &= k_1[A]_{2,\text{eq}}[B]_{2,\text{eq}} - k_{-1}[P]_{2,\text{eq}} \\ &\quad - \{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}\}\Delta[P] + O(\Delta[P]^2) \end{aligned}$$

Show that the first terms on the right side of this equation cancel and that Equations 28.53 and 28.54 result.

After the temperature jump to the new equilibrium state, we can write Equation 1 in terms of the new equilibrium state and the changes in concentration:

$$\frac{d([P]_{2,\text{eq}} + \Delta[P])}{dt} = k_1([A]_{2,\text{eq}} + \Delta[A])([B]_{2,\text{eq}} + \Delta[B]) - k_{-1}([P]_{2,\text{eq}} + \Delta[P])$$

Because  $[P]_{2,\text{eq}}$  does not vary with time and  $\Delta[A] = \Delta[B] = -\Delta[P]$ , we can simplify the above expression to

$$\begin{aligned} \frac{d\Delta[P]}{dt} &= k_1([A]_{2,\text{eq}} - \Delta[P])([B]_{2,\text{eq}} - \Delta[P]) - k_{-1}([P]_{2,\text{eq}} + \Delta[P]) \\ \frac{d\Delta[P]}{dt} &= k_1[A]_{2,\text{eq}}[B]_{2,\text{eq}} - k_{-1}[P]_{2,\text{eq}} - \{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}\}\Delta[P] + O((\Delta[P])^2) \end{aligned}$$

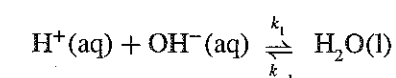
At equilibrium,  $d[P]/dt = 0$ , so  $k_{-1}[P]_{2,\text{eq}} = k_1[A]_{2,\text{eq}}[B]_{2,\text{eq}}$  and the first terms on the right hand side of the equation cancel. Then (disregarding second-order and higher terms in  $\Delta[P]$ )

$$\begin{aligned} \frac{d\Delta[P]}{dt} &= -\{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}\}\Delta[P]_{2,\text{eq}} \\ \frac{d\Delta[P]}{\Delta[P]} &= -dt\{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}\} \\ \ln \frac{\Delta[P]}{\Delta[P]_0} &= -t\{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}\} \\ \Delta[P] &= \Delta[P]_0 e^{-t/\tau} \end{aligned}$$

where

$$\tau = \frac{1}{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}}$$

28–34. The equilibrium constant for the reaction



at 25°C is  $K_c = [\text{H}_2\text{O}]/[\text{H}^+][\text{OH}^-] = 5.49 \times 10^{15} \text{ mol}^{-1} \cdot \text{dm}^3$ . The time-dependent conductivity of the solution following a temperature jump to a final temperature of 25°C shows a relaxation time of  $\tau = 3.7 \times 10^{-5} \text{ s}$ . Determine the values of the rate constants  $k_1$  and  $k_{-1}$ . At 25°C, the density of water is  $\rho = 0.997 \text{ g} \cdot \text{cm}^{-3}$ .

The concentration of water at 25°C is

$$\frac{0.997 \text{ g} \cdot \text{cm}^{-3}}{18.015 \text{ g} \cdot \text{mol}^{-1}} \left( \frac{10 \text{ cm}}{1 \text{ dm}} \right)^3 = 55.3 \text{ mol} \cdot \text{dm}^{-3}$$

Let  $x$  be the number of moles of water that dissociate per liter. Then, at equilibrium,  $[\text{H}_2\text{O}] = 55.3 \text{ mol} \cdot \text{dm}^{-3} - x$ , and  $[\text{H}^+] = [\text{OH}^-] = x$ . We can use the  $K_c$  given in the problem and these values to write

$$K_c = \frac{[\text{H}_2\text{O}]}{[\text{H}^+][\text{OH}^-]} = \frac{55.3 \text{ mol} \cdot \text{dm}^{-3} - x}{x^2}$$

$$5.49 \times 10^{15} \text{ mol}^{-1} \cdot \text{dm}^3 = \frac{55.3 \text{ mol} \cdot \text{dm}^{-3} - x}{x^2}$$

$$x = 1.00 \times 10^{-7} \text{ dm}^{-3} \cdot \text{mol}$$

where we have taken the positive root as  $x$ . Then  $[\text{OH}^-] = [\text{H}^+] = 1.00 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ . We also note that  $K_c = k_1/k_{-1}$ , so

$$k_1 = 5.49 \times 10^{15} \text{ mol}^{-1} \cdot \text{dm}^3 k_{-1} \quad (1)$$

We can use Equation 28.54 to write

$$k_{-1} + k_1([\text{H}^+] + [\text{OH}^-]) = \frac{1}{\tau}$$

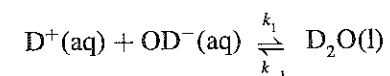
Substituting for  $[\text{H}^+]$ ,  $[\text{OH}^-]$ , and  $k_1$ , we find

$$k_{-1} = \frac{1}{(3.7 \times 10^{-5} \text{ s})[1 + (5.49 \times 10^{15} \text{ mol}^{-1} \cdot \text{dm}^3)(2.00 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3})]}$$

$$= 2.5 \times 10^{-5} \text{ s}^{-1}$$

and (substituting back into Equation 1)  $k_1 = 1.4 \times 10^{11} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ .

### 28–35. The equilibrium constant for the reaction



at 25°C is  $K_c = 4.08 \times 10^{16} \text{ mol}^{-1} \cdot \text{dm}^3$ . The rate constant  $k_{-1}$  is independently found to be  $2.52 \times 10^{-6} \text{ s}^{-1}$ . What do you predict for the observed relaxation time for a temperature-jump experiment to a final temperature of 25°C? The density of  $\text{D}_2\text{O}$  is  $\rho = 1.104 \text{ g} \cdot \text{cm}^{-3}$  at 25°C.

The concentration of  $\text{D}_2\text{O}$  at 25°C is

$$\frac{1.104 \text{ g} \cdot \text{cm}^{-3}}{20.027 \text{ g} \cdot \text{mol}^{-1}} \left( \frac{10 \text{ cm}}{1 \text{ dm}} \right)^3 = 55.13 \text{ mol} \cdot \text{dm}^{-3}$$

Let  $x$  be the number of moles of  $\text{D}_2\text{O}$  that dissociate per liter. Then, at equilibrium,  $[\text{D}_2\text{O}] = 55.13 \text{ mol} \cdot \text{dm}^{-3} - x$ , and  $[\text{D}^+] = [\text{OD}^-] = x$ . We can use the  $K_c$  given in the problem and these values to write

$$K_c = \frac{[\text{H}_2\text{O}]}{[\text{H}^+][\text{OH}^-]} = \frac{55.13 \text{ mol} \cdot \text{dm}^{-3} - x}{x^2}$$

$$4.08 \times 10^{16} \text{ mol}^{-1} \cdot \text{dm}^3 = \frac{55.13 \text{ mol} \cdot \text{dm}^{-3} - x}{x^2}$$

$$x = 3.68 \times 10^{-8} \text{ dm}^{-3} \cdot \text{mol}$$

where we have taken the positive root as  $x$ . Then  $[\text{OD}^-] = [\text{D}^+] = 3.68 \times 10^{-8} \text{ mol} \cdot \text{dm}^{-3}$ . We can also write  $K_c$  as  $k_1/k_{-1}$ , so (using the given value of  $k_{-1}$ )

$$k_1 = k_{-1}K_c = (2.52 \times 10^{-6} \text{ s}^{-1})(4.08 \times 10^{16} \text{ mol}^{-1} \cdot \text{dm}^3) = 1.03 \times 10^{11} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$$

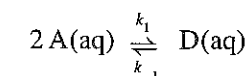
We can now use Equation 28.54 to write

$$\tau = \frac{1}{k_{-1} + k_1([\text{D}^+] + [\text{OD}^-])}$$

$$= \frac{1}{2.52 \times 10^{-6} \text{ s}^{-1} + (1.03 \times 10^{11} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1})(7.36 \times 10^{-8} \text{ mol} \cdot \text{dm}^{-3})}$$

$$= 1.32 \times 10^{-4} \text{ s}$$

### 28–36. Consider the chemical reaction described by



If we assume the forward reaction is second order and the reverse reaction is first order, the rate law is given by

$$\frac{d[\text{D}]}{dt} = k_1[\text{A}]^2 - k_{-1}[\text{D}] \quad (1)$$

Now consider the response of this chemical reaction to a temperature jump. Let  $[\text{A}] = [\text{A}]_{2,\text{eq}} + \Delta[\text{A}]$  and  $[\text{D}] = [\text{D}]_{2,\text{eq}} + \Delta[\text{D}]$ , where the subscript “2,eq” refers to the new equilibrium state. Now use the fact that  $\Delta[\text{A}] = -2\Delta[\text{D}]$  to show that Equation 1 becomes

$$\frac{d\Delta[\text{D}]}{dt} = -(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})\Delta[\text{D}] + O(\Delta[\text{D}]^2)$$

Show that if we ignore the  $O(\Delta[\text{D}]^2)$  term, then

$$\Delta[\text{D}] = \Delta[\text{D}]_0 e^{-t/\tau}$$

where  $\tau = 1/(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})$ .

We let  $[\text{A}] = [\text{A}]_{2,\text{eq}} + \Delta[\text{A}]$  and  $[\text{D}] = [\text{D}]_{2,\text{eq}} + \Delta[\text{D}]$  in Equation 1:

$$\frac{d[\text{D}]}{dt} = k_1[\text{A}]^2 - k_{-1}[\text{D}]$$

$$\frac{d([\text{D}]_{2,\text{eq}} + \Delta[\text{D}])}{dt} = k_1([\text{A}]_{2,\text{eq}} + \Delta[\text{A}])^2 - k_{-1}([\text{D}]_{2,\text{eq}} + \Delta[\text{D}])$$

Now use the relation  $\Delta[A] = -2\Delta[D]$  to write

$$\begin{aligned}\frac{d\Delta[D]}{dt} &= k_1([A]_{2,\text{eq}} - 2\Delta[D])^2 - k_{-1}([D]_{2,\text{eq}} + \Delta[D]) \\ &= k_1[A]_{2,\text{eq}}^2 - 4k_1[A]_{2,\text{eq}}\Delta[D] - k_{-1}[D]_{2,\text{eq}} - k_{-1}\Delta[D] + O\{(\Delta[D])^2\}\end{aligned}$$

At equilibrium,  $d[D]/dt = 0$ , so (from Equation 1)  $k_{-1}[D]_{2,\text{eq}} = k_1[A]_{2,\text{eq}}^2$ . Then

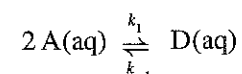
$$\frac{d\Delta[D]}{dt} = -(4k_1[A]_{2,\text{eq}} + k_{-1})\Delta[D] + O\{(\Delta[D])^2\}$$

Ignoring second-order and higher terms in  $\Delta[D]$  and integrating gives

$$\begin{aligned}\frac{d\Delta[D]}{dt} &= -(4k_1[A]_{2,\text{eq}} + k_{-1})\Delta[D] \\ \frac{d\Delta[D]}{\Delta[D]} &= -dt(4k_1[A]_{2,\text{eq}} + k_{-1}) \\ \ln \frac{\Delta[D]}{\Delta[D]_0} &= t(4k_1[A]_{2,\text{eq}} + k_{-1}) \\ \Delta[D] &= \Delta[D]_0 e^{-t/\tau}\end{aligned}$$

where  $\tau = 1/(4k_1[A]_{2,\text{eq}} + k_{-1})$ .

**28-37.** In Problem 28-36, you showed that the relaxation time for the dimerization reaction



is given by  $\tau = 1/(4k_1[A]_{2,\text{eq}} + k_{-1})$ . Show that this equation can be rewritten as

$$\frac{1}{\tau^2} = k_{-1}^2 + 8k_1k_{-1}[S]_0$$

where  $[S]_0 = 2[D] + [A] = 2[D]_{2,\text{eq}} + [A]_{2,\text{eq}}$ .

We write the equilibrium constant in terms of the rate constants and the concentrations of D and A:

$$\begin{aligned}K &= \frac{[D]_{2,\text{eq}}}{[A]_{2,\text{eq}}^2} = \frac{k_1}{k_{-1}} \\ [D]_{2,\text{eq}} &= \frac{[A]_{2,\text{eq}}^2 k_1}{k_{-1}}\end{aligned}\quad (1)$$

Because  $[S]_0$  is a constant,  $[S]_0 = [A]_{2,\text{eq}} + 2[D]_{2,\text{eq}}$ . Substituting for  $[D]_{2,\text{eq}}$  from Equation 1 gives

$$\begin{aligned}[S]_0 &= [A]_{2,\text{eq}} + \frac{2[A]_{2,\text{eq}}^2 k_1}{k_{-1}} \\ k_{-1}[S]_0 &= 2k_1[A]_{2,\text{eq}}^2 + k_{-1}[A]_{2,\text{eq}}\end{aligned}\quad (2)$$

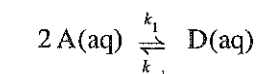
From Problem 28-36, we can write  $1/\tau^2$  as

$$\begin{aligned}\frac{1}{\tau^2} &= (4k_1[A]_{2,\text{eq}} + k_{-1})^2 \\ &= 16k_1^2[A]_{2,\text{eq}}^2 + 8k_1k_{-1}[A]_{2,\text{eq}} + k_{-1}^2 \\ &= 8k_1(2k_1[A]_{2,\text{eq}}^2 + k_{-1}[A]_{2,\text{eq}}) + k_{-1}^2\end{aligned}$$

Substituting from Equation 2, we obtain

$$\frac{1}{\tau^2} = 8k_1k_{-1}[S]_0 + k_{-1}^2$$

**28-38.** The first step in the assembly of the protein yeast phosphoglycerate mutase is a reversible dimerization of a polypeptide,



where A is the polypeptide and D is the dimer. Suppose that a  $1.43 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$  solution of A is prepared and allowed to come to equilibrium at 280 K. Once equilibrium is achieved, the temperature of the solution is jumped to 293 K. The rate constants  $k_1$  and  $k_{-1}$  for the dimerization reaction at 293 K are  $6.25 \times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  and  $6.00 \times 10^{-3} \text{ s}^{-1}$ , respectively. Calculate the value of the relaxation time observed in the experiment. (Hint: See Problem 28-37.)

From Problem 28-37, we have

$$\frac{1}{\tau^2} = 8k_1k_{-1}[S]_0 + k_{-1}^2$$

We are given  $[A]_0 = 1.43 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ . Because  $[D]_0 = 0$ ,  $[A]_0 = [A]_{2,\text{eq}} + 2[D]_{2,\text{eq}}$ , so  $[S]_0 = 1.43 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ . Then

$$\begin{aligned}\frac{1}{\tau^2} &= 8(6.25 \times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1})(6.00 \times 10^{-3} \text{ s}^{-1})(1.43 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}) + (6.00 \times 10^{-3} \text{ s}^{-1})^2 \\ \frac{1}{\tau^2} &= 4.33 \times 10^{-3} \text{ s}^{-2} \\ \tau &= 15.2 \text{ s}\end{aligned}$$

**28-39.** Does the Arrhenius A factor always have the same units as the reaction rate constant?

Yes. The Arrhenius equation is

$$k = Ae^{-E_a/RT} \quad (28.57)$$

Because the exponential term is unitless,  $k$  and  $A$  have the same units.

**28-40.** Use the results of Problems 28-26 and 28-27 to calculate the values of  $E_a$  and  $A$  for the decomposition of uranyl nitrate.

We can use the expression from Example 28-8,

$$E_a = R \left( \frac{T_1 T_2}{T_1 - T_2} \right) \ln \frac{k(T_1)}{k(T_2)}$$

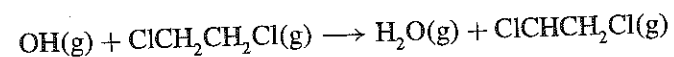
In Problems 28–26 and 28–27, we found that  $k = 8.82 \times 10^{-3} \text{ min}^{-1}$  at 298 K and that  $k = 0.0505 \text{ min}^{-1}$  at 623 K for the decomposition of uranyl nitrate. Substituting into the above equation, we find

$$E_a = (8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \left[ \frac{(298 \text{ K})(623 \text{ K})}{298 \text{ K} - 623 \text{ K}} \right] \ln \frac{8.82 \times 10^{-3} \text{ min}^{-1}}{0.0505 \text{ min}^{-1}} = 8290 \text{ J} \cdot \text{mol}^{-1}$$

The value of  $A$  is given by Equation 28.57. Using the values at 298 K, we find that

$$A = ke^{E_a/RT} = (8.82 \times 10^{-3} \text{ min}^{-1}) \exp \left[ \frac{8290 \text{ J} \cdot \text{mol}^{-1}}{(8.315 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} \right] = 0.250 \text{ min}^{-1}$$

28–41. The experimental rate constants for the reaction described by



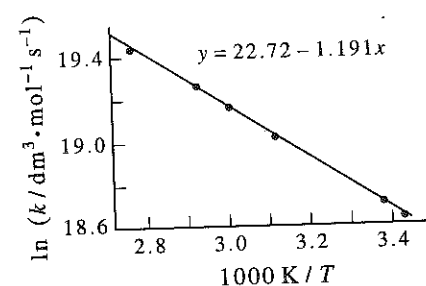
at various temperatures are tabulated below.

$T/\text{K}$	292	296	321	333	343	363
$k/10^8 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	1.24	1.32	1.81	2.08	2.29	2.75

Determine the values of the Arrhenius parameters  $A$  and  $E_a$  for this reaction.

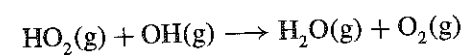
We can write the Arrhenius equation as

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (28.56)$$



The best-fit line to a plot of  $\ln k$  versus  $1/T$  will have an intercept of  $\ln A$  and a slope of  $-E_a/R$ . Here, the best fit of the experimental data gives  $A = 7.37 \times 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and  $E_a = 9.90 \text{ kJ} \cdot \text{mol}^{-1}$ .

28–42. The Arrhenius parameters for the reaction described by



are  $A = 5.01 \times 10^{10} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and  $E_a = 4.18 \text{ kJ} \cdot \text{mol}^{-1}$ . Determine the value of the rate constant for this reaction at 298 K.

We can use Equation 28.57:

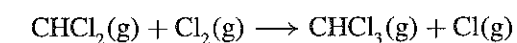
$$\begin{aligned} k &= Ae^{-E_a/RT} \\ &= (5.01 \times 10^{10} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}) \exp \left[ -\frac{4180 \text{ J} \cdot \text{mol}^{-1}}{(8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} \right] \\ &= 9.27 \times 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \end{aligned}$$

28–43. At what temperature will the reaction described in Problem 28–42 have a rate constant that is twice that at 298 K?

Again, use Equation 28.57:

$$\begin{aligned} T &= \frac{-E_a}{R} \frac{1}{\ln(k/A)} \\ &= \frac{-4180 \text{ J} \cdot \text{mol}^{-1}}{8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \frac{1}{\ln[2(9.27 \times 10^9)/5.01 \times 10^{10}]} \\ &= 506 \text{ K} \end{aligned}$$

28–44. The rate constants for the reaction



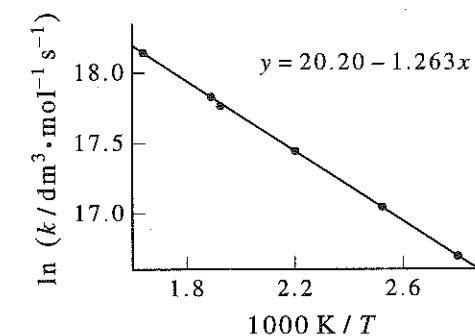
at different temperatures are tabulated below

$T/\text{K}$	357	400	458	524	533	615
$k/10^7 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	1.72	2.53	3.82	5.20	5.61	7.65

Calculate the values of the Arrhenius parameters  $A$  and  $E_a$  for this reaction.

We can write the Arrhenius equation as

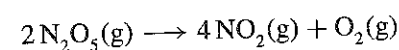
$$\ln k = \ln A - \frac{E_a}{RT} \quad (28.56)$$



The best-fit line to a plot of  $\ln k$  versus  $1/T$  will have an intercept of  $\ln A$  and a slope of  $-E_a/R$ . Here, the best fit of the experimental data gives  $A = 5.93 \times 10^8 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  and  $E_a = 10.5 \text{ kJ} \cdot \text{mol}^{-1}$ .



28-45. The rate constant for the chemical reaction

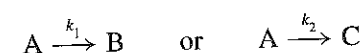


doubles from 22.50°C to 27.47°C. Determine the activation energy of the reaction. Assume the pre-exponential factor is independent of temperature.

We can use the expression for  $E_a$  derived in Example 28-8:

$$\begin{aligned} E_a &= R \left( \frac{T_1 T_2}{T_1 - T_2} \right) \ln \frac{k(T_1)}{k(T_2)} \\ &= (8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \left[ \frac{(295.65 \text{ K})(300.62 \text{ K})}{(295.65 - 300.62) \text{ K}} \right] \ln \frac{1}{2} \\ &= 103.1 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

28-46. Show that if A reacts to form either B or C according to



then  $E_a$ , the observed activation energy for the disappearance of A, is given by

$$E_a = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

where  $E_1$  is the activation energy for the first reaction and  $E_2$  is the activation energy for the second reaction.

The Arrhenius equations for each reaction are (Equation 28.57)

$$k_1 = A_1 e^{-E_1/RT} \quad \text{and} \quad k_2 = A_2 e^{-E_2/RT}$$

The observed rate constant for the disappearance of A is going to be the sum of  $k_1$  and  $k_2$ . Therefore, the Arrhenius equation for the net effect of both reactions can be written as (Equation 28.55)

$$\frac{d \ln(k_1 + k_2)}{dT} = \frac{E_a}{RT^2}$$

Substituting for  $k_1$  and  $k_2$  and taking the derivative gives

$$\begin{aligned} \frac{1}{k_1 + k_2} \frac{d}{dT} (A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}) &= \frac{E_a}{RT^2} \\ \frac{1}{k_1 + k_2} \left( \frac{A_1 E_1}{RT^2} e^{-E_1/RT} + \frac{A_2 E_2}{RT^2} e^{-E_2/RT} \right) &= \frac{E_a}{RT^2} \\ \frac{1}{k_1 + k_2} (A_1 E_1 e^{-E_1/RT} + A_2 E_2 e^{-E_2/RT}) &= E_a \\ \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2} &= E_a \end{aligned}$$

28-47. Cyclohexane interconverts between a "chair" and a "boat" structure. The activation parameters for the reaction from the chair to the boat form of the molecule are  $\Delta^\ddagger H^\circ = 31.38 \text{ kJ} \cdot \text{mol}^{-1}$  and

$\Delta^\ddagger S^\circ = 16.74 \text{ J} \cdot \text{K}^{-1}$ . Calculate the standard Gibbs energy of activation and the rate constant for this reaction at 325 K.

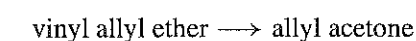
We can use Equation 28.73 to find  $\Delta^\ddagger G^\circ$ :

$$\begin{aligned} \Delta^\ddagger G^\circ &= \Delta^\ddagger H^\circ - T \Delta^\ddagger S^\circ \\ &= 31.38 \text{ kJ} \cdot \text{mol}^{-1} - (325 \text{ K})(16.74 \text{ J} \cdot \text{mol}^{-1}) \\ &= 25.94 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The rate constant is given by Equation 28.72 ( $c^\circ = 1$ ):

$$\begin{aligned} k &= \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ/RT} \\ &= (6.77 \times 10^{12} \text{ s}^{-1}) \exp \left[ \frac{-25940 \text{ J} \cdot \text{mol}^{-1}}{(8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(325 \text{ K})} \right] \\ &= 4.59 \times 10^8 \text{ s}^{-1} \end{aligned}$$

28-48. The gas-phase rearrangement reaction



has a rate constant of  $6.015 \times 10^{-5} \text{ s}^{-1}$  at 420 K and a rate constant of  $2.971 \times 10^{-3} \text{ s}^{-1}$  at 470 K. Calculate the values of the Arrhenius parameters  $A$  and  $E_a$ . Calculate the values of  $\Delta^\ddagger H^\circ$  and  $\Delta^\ddagger S^\circ$  at 420 K. (Assume ideal-gas behavior.)

We can use the expression derived in Example 28-8 to find  $E_a$ :

$$\begin{aligned} E_a &= R \left( \frac{T_1 T_2}{T_1 - T_2} \right) \ln \frac{k(T_1)}{k(T_2)} \\ &= (8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \left[ \frac{(420 \text{ K})(470 \text{ K})}{420 \text{ K} - 470 \text{ K}} \right] \ln \frac{6.015 \times 10^{-5} \text{ s}^{-1}}{2.971 \times 10^{-3} \text{ s}^{-1}} \\ &= 128.0 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Using this value in the Arrhenius equation with the rate constant at 420 K gives

$$6.015 \times 10^{-5} \text{ s}^{-1} = A \exp \left[ -\frac{128000 \text{ J} \cdot \text{mol}^{-1}}{(8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(420 \text{ K})} \right] \quad A = 5.01 \times 10^{11} \text{ s}^{-1}$$

We can write (Equation 28.55)

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2}$$

and, for an ideal-gas system, we also have (Equation 28.76)

$$\frac{d \ln k}{dt} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

For a unimolecular reaction,  $\Delta^\ddagger H^\circ = \Delta^\ddagger U^\circ$ , and so equating these two expressions gives

$$\begin{aligned} \frac{E_a}{RT^2} &= \frac{1}{T} + \frac{\Delta^\ddagger H^\circ}{RT^2} \\ E_a &= RT + \Delta^\ddagger H^\circ \end{aligned}$$

We can solve this equation for  $\Delta^\ddagger H^\circ$  at 420 K:

$$\Delta^\ddagger H^\circ = 128.0 \text{ kJ}\cdot\text{mol}^{-1} - (8.315 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1})(420 \text{ K}) = 124.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Because  $E_a = \Delta^\ddagger H^\circ + RT$  for a reaction of type  $A \rightarrow P$ , Equation 28.80 becomes

$$A = \frac{ek_B T}{h} e^{\Delta^\ddagger S^\circ/R}$$

Solving for  $\Delta^\ddagger S^\circ$  gives

$$\begin{aligned} \Delta^\ddagger S^\circ &= R \ln \left[ \frac{Ah}{ek_B T} \right] \\ &= (8.315 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln \left[ \frac{(4.98 \times 10^{11} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ J}\cdot\text{s})}{e(1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1})(420 \text{ K})} \right] \\ &= -32.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

**28–49.** The kinetics of a chemical reaction can be followed by a variety of experimental techniques, including optical spectroscopy, NMR spectroscopy, conductivity, resistivity, pressure changes, and volume changes. When using these techniques, we do not measure the concentration itself but we know that the observed signal is proportional to the concentration; the exact proportionality constant depends on the experimental technique and the species present in the chemical system. Consider the general reaction given by



where we assume that A is the limiting reagent so that  $[A] \rightarrow 0$  as  $t \rightarrow \infty$ . Let  $p_i$  be the proportionality constant for the contribution of species  $i$  to  $S$ , the measured signal from the instrument. Explain why at any time  $t$  during the reaction,  $S$  is given by

$$S(t) = p_A[A] + p_B[B] + p_Y[Y] + p_Z[Z] \quad (1)$$

Show that the initial and final readings from the instrument are given by

$$S(0) = p_A[A]_0 + p_B[B]_0 + p_Y[Y]_0 + p_Z[Z]_0 \quad (2)$$

and

$$S(\infty) = p_B \left( [B]_0 - \frac{\nu_B}{\nu_A} [A]_0 \right) + p_Y \left( [Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 \right) + p_Z \left( [Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 \right) \quad (3)$$

Combine Equations 1 through 3 to show that

$$[A] = [A]_0 \frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

(Hint: Be sure to express  $[B]$ ,  $[Y]$ , and  $[Z]$  in terms of their initial values,  $[A]$  and  $[A]_0$ .)

Equation 1 holds because the total measured signal is the sum of the signals from each species. Because  $p_i[i]$  is the amount of signal that species  $i$  contributes, we have Equation 1. Initially, therefore, we have

$$S(0) = p_A[A]_0 + p_B[B]_0 + p_Y[Y]_0 + p_Z[Z]_0 \quad (2)$$

As  $t \rightarrow \infty$  (at the time of the final reading),  $[A] \rightarrow 0$ . From the stoichiometry of the reaction, we know that at  $t = \infty$ ,  $\nu_B[A]_0/\nu_A$  moles of B have reacted,  $\nu_Y[A]_0/\nu_A$  moles of Y have been produced, and  $\nu_Z[A]_0/\nu_A$  moles of Z have been produced. We then have

$$S(\infty) = p_B \left( [B]_0 - \frac{\nu_B}{\nu_A} [A]_0 \right) + p_Y \left( [Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 \right) + p_Z \left( [Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 \right) \quad (3)$$

At time  $t$ , when the concentration of A is  $[A]$ ,

$$[B] = [B]_\infty + \frac{\nu_B}{\nu_A} [A]$$

$$[Y] = [Y]_\infty - \frac{\nu_Y}{\nu_A} [A]$$

$$[Z] = [Z]_\infty - \frac{\nu_Z}{\nu_A} [A]$$

We can combine these equations with Equations 1 and 3 to find

$$\begin{aligned} S(t) &= p_A[A] + p_B \left( [B]_0 - \frac{\nu_B}{\nu_A} [A]_0 + \frac{\nu_B}{\nu_A} [A] \right) \\ &\quad + p_Y \left( [Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 - \frac{\nu_Y}{\nu_A} [A] \right) + p_Z \left( [Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 - \frac{\nu_Z}{\nu_A} [A] \right) \end{aligned}$$

Then

$$S(t) - S(\infty) = p_A[A] + \frac{\nu_B}{\nu_A} p_B[A] - \frac{\nu_Y}{\nu_A} p_Y[A] - \frac{\nu_Z}{\nu_A} p_Z[A]$$

$$S(0) - S(\infty) = p_A[A]_0 + \frac{\nu_B}{\nu_A} p_B[A]_0 - \frac{\nu_Y}{\nu_A} p_Y[A]_0 - \frac{\nu_Z}{\nu_A} p_Z[A]_0$$

and

$$\frac{S(t) - S(\infty)}{S(0) - S(\infty)} = \frac{[A]}{[A]_0}$$

**28–50.** Use the result of Problem 28–49 to show that for the first-order rate law,  $v = k[A]$ , the time-dependent signal is given by

$$S(t) = S(\infty) + [S(0) - S(\infty)]e^{-kt}$$

For the first-order rate law

$$[A] = [A]_0 e^{-kt} \quad (28.23)$$

We can use the final result of Problem 28–49 to write this as

$$\frac{S(t) - S(\infty)}{S(0) - S(\infty)} = \frac{[A]}{[A]_0} = e^{-kt}$$

or

$$S(t) = S(\infty) + [S(0) - S(\infty)]e^{-kt}$$

**28-51.** Use the result of Problem 28-49 to show that for the second-order rate law,  $v = k[A]^2$ , the time-dependent signal is given by

$$S(t) = S(\infty) + \frac{S(0) - S(\infty)}{1 + [A]_0 kt}$$

For the second order rate law

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad (28.33)$$

We can write this equation in terms of  $[A]/[A]_0$ :

$$\begin{aligned} [A] &= \frac{[A]_0}{1 + [A]_0 kt} \\ \frac{[A]}{[A]_0} &= \frac{1}{1 + [A]_0 kt} \end{aligned}$$

and then use the final result of Problem 28-49 to write

$$\frac{S(t) - S(\infty)}{S(0) - S(\infty)} = \frac{[A]}{[A]_0} = \frac{1}{1 + [A]_0 kt}$$

or

$$S(t) = S(\infty) + \frac{S(0) - S(\infty)}{1 + [A]_0 kt}$$

**28-52.** Because there is a substantial increase in the volume of the solution as the reaction proceeds, the decomposition of diacetone alcohol can be followed by a dilatometer, a device that measures the volume of a sample as a function of time. The instrument readings at various times are tabulated below.

Time/s	0	24.4	35.0	48.0	64.8	75.8	133.4	$\infty$
$S/\text{arbitrary units}$	8.0	20.0	24.0	28.0	32.0	34.0	40.0	43.3

Use the expressions derived in Problems 28-50 and 28-51 to determine if the decomposition reaction is a first- or second-order process.

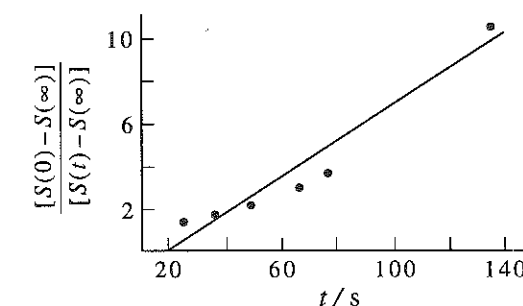
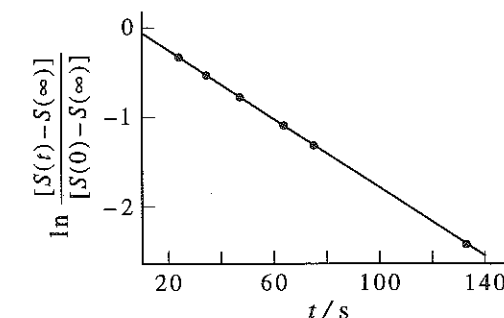
If the decomposition reaction is a first-order process, then

$$\ln \frac{S(t) - S(\infty)}{S(0) - S(\infty)} = -kt$$

and a plot of  $\ln[S(t) - S(\infty)]/[S(0) - S(\infty)]$  versus  $t$  will be linear. If the decomposition reaction is a second-order process, then

$$1 + [A]_0 kt = \left[ \frac{S(t) - S(\infty)}{S(0) - S(\infty)} \right]^{-1}$$

and a plot of  $[S(0) - S(\infty)]/[S(t) - S(\infty)]$  versus  $t$  will be linear.



This is a first-order process.

**28-54.** In Problem 28-49, we assumed that A reacted completely so that  $[A] \rightarrow 0$  as  $t \rightarrow \infty$ . Show that if the reaction does not go to completion but establishes an equilibrium instead, then

$$[A] = [A]_{2,\text{eq}} + ([A]_0 - [A]_{2,\text{eq}}) \frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

where  $[A]_{2,\text{eq}}$  is the equilibrium concentration of A.

Because  $S(t)$  and  $S(0)$  are the same as in Problem 28-49, we can still use Equations 1 and 2 from that problem. If the reaction establishes an equilibrium, Equation 3 becomes

$$\begin{aligned} S(\infty) &= p_A [A]_{2,\text{eq}} + p_B \left( [B]_0 - \frac{\nu_B}{\nu_A} [A]_0 + \frac{\nu_B}{\nu_A} [A]_{2,\text{eq}} \right) + p_Y \left( [Y]_0 + \frac{\nu_Y}{\nu_A} [A]_0 - \frac{\nu_Y}{\nu_A} [A]_{2,\text{eq}} \right) \\ &\quad + p_Z \left( [Z]_0 + \frac{\nu_Z}{\nu_A} [A]_0 - \frac{\nu_Z}{\nu_A} [A]_{2,\text{eq}} \right) \end{aligned}$$

Then

$$\begin{aligned} S(t) - S(\infty) &= p_A ([A] - [A]_{2,\text{eq}}) + p_B \left( \frac{\nu_B}{\nu_A} [A] - \frac{\nu_B}{\nu_A} [A]_{2,\text{eq}} \right) \\ &\quad - p_Y \left( \frac{\nu_Y}{\nu_A} [A] - \frac{\nu_Y}{\nu_A} [A]_{2,\text{eq}} \right) - p_Z \left( \frac{\nu_Z}{\nu_A} [A] - \frac{\nu_Z}{\nu_A} [A]_{2,\text{eq}} \right) \\ &= \left( p_A + \frac{\nu_B}{\nu_A} p_B - \frac{\nu_Y}{\nu_A} p_Y - \frac{\nu_Z}{\nu_A} p_Z \right) ([A] - [A]_{2,\text{eq}}) \end{aligned}$$

and

$$\begin{aligned} S(0) - S(\infty) &= p_A ([A]_0 - [A]_{2,\text{eq}}) + p_B \left( \frac{\nu_B}{\nu_A} [A]_0 - \frac{\nu_B}{\nu_A} [A]_{2,\text{eq}} \right) \\ &\quad - p_Y \left( \frac{\nu_Y}{\nu_A} [A]_0 - \frac{\nu_Y}{\nu_A} [A]_{2,\text{eq}} \right) - p_Z \left( \frac{\nu_Z}{\nu_A} [A]_0 - \frac{\nu_Z}{\nu_A} [A]_{2,\text{eq}} \right) \\ &= \left( p_A + \frac{\nu_B}{\nu_A} p_B - \frac{\nu_Y}{\nu_A} p_Y - \frac{\nu_Z}{\nu_A} p_Z \right) ([A]_0 - [A]_{2,\text{eq}}) \end{aligned}$$

Dividing the first equation by the second gives

$$\frac{S(t) - S(\infty)}{S(0) - S(\infty)} = \frac{[A] - [A]_{2,\text{eq}}}{[A]_0 - [A]_{2,\text{eq}}}$$

or

$$[A] = [A]_{2,\text{eq}} + ([A]_0 - [A]_{2,\text{eq}}) \frac{S(t) - S(\infty)}{S(0) - S(\infty)}$$

## Chemical Kinetics II: Reaction Mechanisms

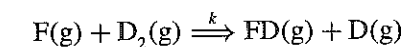
### PROBLEMS AND SOLUTIONS

29-1. Give the units of the rate constant for a unimolecular, bimolecular, and termolecular reaction.

Since  $v$  is in units of  $\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1}$ , the units of  $k$  are

$$\begin{aligned} k_{\text{unimolecular}} &: (\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1})(\text{dm}^3 \cdot \text{mol}^{-1}) = \text{s}^{-1} \\ k_{\text{bimolecular}} &: (\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1})(\text{dm}^3 \cdot \text{mol}^{-1})^2 = \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \\ k_{\text{termolecular}} &: (\text{mol} \cdot \text{dm}^{-3} \cdot \text{s}^{-1})(\text{dm}^3 \cdot \text{mol}^{-1})^3 = \text{dm}^6 \cdot \text{mol}^{-2} \cdot \text{s}^{-1} \end{aligned}$$

29-2. Determine the rate law for the following reaction



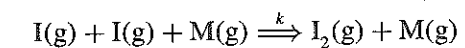
Give the units of  $k$ . Determine the molecularity of this reaction.

Because this is an elementary reaction, the rate law is

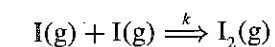
$$v = k[\text{F}][\text{D}_2]$$

This is a bimolecular reaction, so the units of  $k$  are  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ .

29-3. Determine the rate law for the reaction



where M is any molecule present in the reaction container. Give the units of  $k$ . Determine the molecularity of this reaction. Is this reaction identical to



Explain.

Because this is an elementary reaction, the rate law is

$$v = k[\text{M}][\text{I}]^2$$