

25 The rates of chemical reactions

Solutions to exercises

Discussion questions

- E25.1(b)** The determination of a rate law is simplified by the isolation method in which the concentrations of all the reactants except one are in large excess. If B is in large excess, for example, then to a good approximation its concentration is constant throughout the reaction. Although the true rate law might be $v = k[A][B]$, we can approximate [B] by $[B]_0$ and write

$$v = k'[A] \quad k' = k[B]_0 \quad [25.8]$$

which has the form of a first-order rate law. Because the true rate law has been forced into first-order form by assuming that the concentration of B is constant, it is called a pseudofirst-order rate law. The dependence of the rate on the concentration of each of the reactants may be found by isolating them in turn (by having all the other substances present in large excess), and so constructing a picture of the overall rate law.

In the method of initial rates, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants. We shall suppose that the rate law for a reaction with A isolated is $v = k[A]^a$; then its initial rate, v_0 is given by the initial values of the concentration of A, and we write $v_0 = k[A]_0^a$. Taking logarithms gives:

$$\log v_0 = \log k + a \log[A]_0 \quad [25.9]$$

For a series of initial concentrations, a plot of the logarithms of the initial rates against the logarithms of the initial concentrations of A should be a straight line with slope a .

The method of initial rates might not reveal the full rate law, for the products may participate in the reaction and affect the rate. For example, products participate in the synthesis of HBr, where the full rate law depends on the concentration of HBr. To avoid this difficulty, the rate law should be fitted to the data throughout the reaction. The fitting may be done, in simple cases at least, by using a proposed rate law to predict the concentration of any component at any time, and comparing it with the data.

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. Even the most complex rate laws may be integrated numerically. However, in a number of simple cases analytical solutions are easily obtained, and prove to be very useful. These are summarized in Table 25.3. In order to determine the rate law, one plots the right hand side of the integrated rate laws shown in the table against t in order to see which of them results in a straight line through the origin. The one that does is the correct rate law.

- E25.2(b)** The rate-determining step is not just the slowest step: it must be slow *and* be a crucial gateway for the formation of products. If a faster reaction can also lead to products, then the slowest step is irrelevant because the slow reaction can then be side-stepped. The rate-determining step is like a slow ferry crossing between two fast highways: the overall rate at which traffic can reach its destination is determined by the rate at which it can make the ferry crossing.

If the first step in a mechanism is the slowest step with the highest activation energy, then it is rate-determining, and the overall reaction rate is equal to the rate of the first step because all subsequent steps are so fast that once the first intermediate is formed it results immediately in the formation

of products. Once over the initial barrier, the intermediates cascade into products. However, a rate-determining step may also stem from the low concentration of a crucial reactant or catalyst and need not correspond to the step with highest activation barrier. A rate-determining step arising from the low activity of a crucial enzyme can sometimes be identified by determining whether or not the reactants and products for that step are in equilibrium: if the reaction is not at equilibrium it suggests that the step may be slow enough to be rate-determining.

E25.3(b) The parameter A , which corresponds to the intercept of the line at $1/T = 0$ (at infinite temperature), is called the pre-exponential factor or the frequency factor. The parameter E_a , which is obtained from the slope of the line ($-E_a/R$), is called the activation energy. Collectively, the two quantities are called the Arrhenius parameters.

The temperature dependence of some reactions is not Arrhenius-like, in the sense that a straight line is not obtained when $\ln k$ is plotted against $1/T$. However, it is still possible to define an activation energy as

$$E_a = RT^2 \left(\frac{d \ln k}{dT} \right)$$

This definition reduces to the earlier one (as the slope of a straight line) for a temperature-independent activation energy. However, this latter definition is more general, because it allows E_a to be obtained from the slope (at the temperature of interest) of a plot of $\ln k$ against $1/T$ even if the Arrhenius plot is not a straight line. Non-Arrhenius behaviour is sometimes a sign that quantum mechanical tunnelling is playing a significant role in the reaction.

E25.4(b) The expression $k = k_a k_b [A]/(k_b + k'_a [A])$ for the effective rate constant of a unimolecular reaction $A \rightarrow P$ is based on the validity of the assumption of the existence of the pre-equilibrium $A + A \rightleftharpoons A^* + A (k_a, k'_a)$. This can be a good assumption if both k_a and k'_a are much larger than k_b . The expression for the effective rate-constant, k , can be rearranged to

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a [A]}$$

Hence, a test of the theory is to plot $1/k$ against $1/[A]$, and to expect a straight line. Another test is based on the prediction from the Lindemann–Hinshelwood mechanism that as the concentration (and therefore the partial pressure) of A is reduced, the reaction should switch to overall second order kinetics. Whereas the mechanism agrees in general with the switch in order of unimolecular reactions, it does not agree in detail. A typical graph of $1/k$ against $1/[A]$ has a pronounced curvature, corresponding to a larger value of k (a smaller value of $1/k$) at high pressures (low $1/[A]$) than would be expected by extrapolation of the reasonably linear low pressure (high $1/[A]$) data.

Numerical exercises

E25.5(b) Rate of reaction = $-\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{2} \frac{d[D]}{dt} = 1.00 \text{ mol L}^{-1} \text{ s}^{-1}$ so

$$\text{Rate of consumption of A} = \boxed{1.0 \text{ mol L}^{-1} \text{ s}^{-1}}$$

$$\text{Rate of consumption of B} = \boxed{3.0 \text{ mol L}^{-1} \text{ s}^{-1}}$$

$$\text{Rate of formation of C} = \boxed{1.0 \text{ mol L}^{-1} \text{ s}^{-1}}$$

$$\text{Rate of formation of D} = \boxed{2.0 \text{ mol L}^{-1} \text{ s}^{-1}}$$

E25.6(b) Rate of consumption of B = $-\frac{d[B]}{dt} = 1.00 \text{ mol L}^{-1} \text{ s}^{-1}$.

$$\text{Rate of reaction} = -\frac{1}{3} \frac{d[B]}{dt} = \boxed{0.33 \text{ mol L}^{-1} \text{ s}^{-1}} = \frac{d[C]}{dt} = \frac{1}{2} \frac{d[D]}{dt} = -\frac{d[A]}{dt}$$

$$\text{Rate of formation of C} = \boxed{0.33 \text{ mol L}^{-1} \text{ s}^{-1}}$$

$$\text{Rate of formation of D} = \boxed{0.66 \text{ mol L}^{-1} \text{ s}^{-1}}$$

$$\text{Rate of consumption of A} = \boxed{0.33 \text{ mol L}^{-1} \text{ s}^{-1}}$$

E25.7(b) The dimensions of k are

$$\frac{\text{dim of } v}{(\text{dim of } [A]) \times (\text{dim of } [B])^2} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^3}$$

$$= \text{length}^6 \times \text{amount}^{-2} \times \text{time}^{-1}$$

In mol, L, s units, the units of k are $\boxed{\text{L}^2 \text{ mol}^{-2} \text{ s}^{-1}}$

(a) $v = -\frac{d[A]}{dt} = k[A][B]^2$ so $\boxed{\frac{d[A]}{dt} = -k[A][B]^2}$

(b) $v = \frac{d[C]}{dt}$ so $\boxed{\frac{d[C]}{dt} = k[A][B]^2}$

E25.8(b) The dimensions of k are

$$\frac{\text{dim of } v}{\text{dim of } [A] \times \text{dim of } [B] \times (\text{dim of } [C])^{-1}} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})} = \text{time}^{-1}$$

The units of k are $\boxed{\text{s}^{-1}}$

$$v = \frac{d[C]}{dt} = \boxed{k[A][B][C]^{-1}}$$

E25.9(b) The rate law is

$$v = kp^a = kp_0(1-f)^a$$

where a is the reaction order, and f the fraction reacted (so that $1-f$ is the fraction remaining). Thus

$$\frac{v_1}{v_2} = \frac{kp_0(1-f_1)^a}{kp_0(1-f_2)^a} = \left(\frac{1-f_1}{1-f_2}\right)^a \quad \text{and} \quad a = \frac{\ln(v_1/v_2)}{\ln\left(\frac{1-f_1}{1-f_2}\right)} = \frac{\ln(9.71/7.67)}{\ln\left(\frac{1-0.100}{1-0.200}\right)} = \boxed{2.00}$$

E25.10(b) The half-life changes with concentration, so we know the reaction order is not 1. That the half-life increases with decreasing concentration indicates a reaction order < 1 . Inspection of the data shows the half-life roughly proportional to concentration, which would indicate a reaction order of 0 according to Table 25.3.

More quantitatively, if the reaction order is 0, then

$$t_{1/2} \propto p \quad \text{and} \quad \frac{t_{1/2}^{(1)}}{t_{1/2}^{(2)}} = \frac{p_1}{p_2}$$

We check to see if this relationship holds

$$\frac{t_{1/2}^{(1)}}{t_{1/2}^{(2)}} = \frac{340 \text{ s}}{178 \text{ s}} = 1.91 \quad \text{and} \quad \frac{p_1}{p_2} = \frac{55.5 \text{ kPa}}{28.9 \text{ kPa}} = 1.92$$

so the reaction order is $\boxed{0}$

E25.11(b) The rate law is

$$v = -\frac{1}{2} \frac{d[A]}{dt} = k[A]$$

The half-life formula in the text, however, is based on a rate constant for the rate of change of the reactant. That is, it would be accurate to say

$$t_{1/2} = \frac{\ln 2}{k'}$$

provided the k' here referred to a rate law

$$-\frac{d[A]}{dt} = k'[A] = 2k[A] \quad \text{so} \quad t_{1/2} = \frac{\ln 2}{2(2.78 \times 10^{-7} \text{ s}^{-1})} = \boxed{1.80 \times 10^6 \text{ s}}$$

The concentration of our reactant (pressure in this case) is

$$[A] = [A]_0 e^{-2kt}$$

(a) Therefore, after 10 h, we have

$$[A] = (32.1 \text{ kPa}) \exp[-2 \times (2.78 \times 10^{-7} \text{ s}^{-1}) \times (3.6 \times 10^4 \text{ s})] = \boxed{31.5 \text{ kPa}}$$

(b) and after 50 h, we have

$$[A] = (32.1 \text{ kPa}) \exp[-2 \times (2.78 \times 10^{-7} \text{ s}^{-1}) \times (1.8 \times 10^5 \text{ s})] = \boxed{29.0 \text{ kPa}}$$

E25.12(b) From Table 25.3, we see that for $A + 2B \rightarrow P$ the integrated rate law is

$$kt = \frac{1}{[B]_0 - 2[A]_0} \ln \left[\frac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0} \right]$$

(a) Substituting the data after solving for k

$$k = \frac{1}{(3.6 \times 10^3 \text{ s}) \times (0.080 - 2 \times 0.075) \times (\text{mol L}^{-1})} \times \ln \left[\frac{0.075 \times (0.080 - 0.060)}{(0.075 - 0.030) \times 0.080} \right]$$

$$= \boxed{3.47 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}}$$

(b) The half-life in terms of A is

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

which reduces to

$$\begin{aligned} t_{1/2}(\text{A}) &= \frac{1}{k([\text{B}]_0 - 2[\text{A}]_0)} \ln \left(2 - \frac{2[\text{A}]_0}{[\text{B}]_0} \right) \\ &= \frac{1}{(3.47 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}) \times (-0.070 \text{ mol L}^{-1})} \times \ln \left(2 - \frac{0.150}{0.080} \right) \\ &= 8561 \text{ s} = \boxed{2.4 \text{ h}} \end{aligned}$$

The half-life in terms of B is

$$t_{1/2}(\text{B}) = \frac{1}{k([\text{B}]_0 - 2[\text{A}]_0)} \ln \left[\frac{[\text{A}]_0([\text{B}]_0 - \frac{[\text{B}]_0}{2})}{\left([\text{A}]_0 - \frac{[\text{B}]_0}{4}\right)[\text{B}]_0} \right]$$

which reduces to

$$\begin{aligned} t_{1/2}(\text{B}) &= \frac{1}{k([\text{B}]_0 - 2[\text{A}]_0)} \ln \left(\frac{[\text{A}]_0/2}{[\text{A}]_0 - [\text{B}]_0/4} \right) \\ &= \frac{1}{(3.47 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}) \times (-0.070 \text{ mol L}^{-1})} \times \ln \left(\frac{0.075/2}{0.075 - (0.080/4)} \right) \\ &= 1576 \text{ s} = \boxed{0.44 \text{ h}} \end{aligned}$$

E25.13(b) The dimensions of a second-order rate constant are

$$\frac{\text{dim of } v}{(\text{dim of } [\text{A}])^2} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^2} = \text{length}^3 \times \text{amount}^{-1} \times \text{time}^{-1}$$

In molecule, m, s units, the units of k are $\boxed{\text{m}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$

The dimensions of a second-order rate constant in pressure units are

$$\frac{\text{dim of } v}{(\text{dim of } p)^2} = \frac{\text{pressure} \times \text{time}^{-1}}{(\text{pressure})^2} = \text{pressure}^{-1} \times \text{time}^{-1}$$

In SI units, the pressure unit is $\text{N m}^{-2} = \text{Pa}$, so the units of k are $\boxed{\text{Pa}^{-1} \text{ s}^{-1}}$

The dimensions of a third-order rate constant are

$$\frac{\text{dim of } v}{(\text{dim of } [\text{A}])^3} = \frac{\text{amount} \times \text{length}^{-3} \times \text{time}^{-1}}{(\text{amount} \times \text{length}^{-3})^3} = \text{length}^6 \times \text{amount}^{-2} \times \text{time}^{-1}$$

In molecule, m, s units, the units of k are $\boxed{\text{m}^6 \text{ molecule}^{-2} \text{ s}^{-1}}$

The dimensions of a third-order rate constant in pressure units are

$$\frac{\text{dim of } v}{(\text{dim of } p)^3} = \frac{\text{pressure} \times \text{time}^{-1}}{(\text{pressure})^3} = \text{pressure}^{-2} \times \text{time}^{-1}$$

In SI units, the pressure unit is $\text{N m}^{-2} = \text{Pa}$, so the units of k are $\boxed{\text{Pa}^{-2} \text{s}^{-1}}$

E25.14(b) The integrated rate law is

$$kt = \frac{1}{[\text{B}]_0 - 2[\text{A}]_0} \ln \frac{[\text{A}]_0([\text{B}]_0 - 2[\text{C}])}{([\text{A}]_0 - [\text{C}])[\text{B}]_0}$$

Solving this for $[\text{C}]$ yields

$$[\text{C}] = \frac{[\text{A}]_0[\text{B}]_0\{\exp[kt([\text{B}]_0 - 2[\text{A}]_0)] - 1\}}{[\text{B}]_0 \exp[kt([\text{B}]_0 - 2[\text{A}]_0)] - 2[\text{A}]_0}$$

$$\text{(a)} \quad [\text{C}]/(\text{mol L}^{-1}) = \frac{(0.025) \times (0.150)}{(0.150) \times \exp[(0.21 \text{ s}^{-1}) \times (10 \text{ s}) \times (0.150 - 2 \times 0.025)] - 2(0.025)} \times \{\exp[(0.21 \text{ s}^{-1}) \times (10 \text{ s}) \times (0.150 - 2 \times 0.025)] - 1\}$$

$$[\text{C}] = \boxed{6.5 \times 10^{-3} \text{ mol L}^{-1}}$$

$$\text{(b)} \quad [\text{C}]/(\text{mol L}^{-1}) = \frac{(0.025) \times (0.150)}{(0.150) \times \exp[(0.21 \text{ s}^{-1}) \times (600 \text{ s}) \times (0.150 - 2 \times 0.025)] - 2(0.025)} \times \{\exp[(0.21 \text{ s}^{-1}) \times (600 \text{ s}) \times (0.150 - 2 \times 0.025)] - 1\}$$

$$[\text{C}] = \boxed{0.025 \text{ mol L}^{-1}}$$

E25.15(b) The rate law is

$$v = -\frac{1}{2} \frac{d[\text{A}]}{dt} = k[\text{A}]^3$$

which integrates to

$$2kt = \frac{1}{2} \left(\frac{1}{[\text{A}]^2} - \frac{1}{[\text{A}]_0^2} \right) \quad \text{so} \quad t = \frac{1}{4k} \left(\frac{1}{[\text{A}]^2} - \frac{1}{[\text{A}]_0^2} \right)$$

$$t = \left(\frac{1}{4(3.50 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1})} \right) \times \left(\frac{1}{(0.021 \text{ mol L}^{-1})^2} - \frac{1}{(0.077 \text{ mol L}^{-1})^2} \right)$$

$$= \boxed{1.5 \times 10^6 \text{ s}}$$

E25.16(b) The rate constant is given by

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

so at 30°C it is

$$1.70 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1} = A \exp\left(\frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(24 + 273) \text{ K}]}\right)$$

and at 50°C it is

$$2.01 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1} = A \exp\left(\frac{-E_a}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(37 + 273) \text{ K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} = \exp\left[\left(\frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)\right]$$

$$\text{so } \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) = \left(\frac{-E_a}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)$$

$$\text{and } E_a = -\left(\frac{1}{297 \text{ K}} - \frac{1}{310 \text{ K}}\right)^{-1} \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= 9.9 \times 10^3 \text{ J mol}^{-1} = \boxed{9.9 \text{ kJ mol}^{-1}}$$

With the activation energy in hand, the prefactor can be computed from either rate constant value

$$A = k \exp\left(\frac{E_a}{RT}\right) = (1.70 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{9.9 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (297 \text{ K})}\right)$$

$$= \boxed{0.94 \text{ L mol}^{-1} \text{ s}^{-1}}$$

- E25.17(b)** (a) Assuming that the rate-determining step is the scission of a C—H bond, the ratio of rate constants for the tritiated versus protonated reactant should be

$$\frac{k_T}{k_H} = e^{-\lambda} \quad \text{where } \lambda = \frac{\hbar k_f^{1/2}}{2kT} \left(\frac{1}{\mu_{\text{CH}}^{1/2}} - \frac{1}{\mu_{\text{CT}}^{1/2}}\right)$$

The reduced masses will be roughly 1 u and 3 u respectively, for the protons and ^3H nuclei are far lighter than the rest of the molecule to which they are attached. So

$$\lambda = \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (450 \text{ N m}^{-1})^{1/2}}{2 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \times \left(\frac{1}{(1 \text{ u})^{1/2}} - \frac{1}{(3 \text{ u})^{1/2}}\right)$$

$$\times (1.66 \times 10^{-27} \text{ kg u}^{-1})^{-1/2}$$

$$= 2.8 \quad \text{so} \quad \boxed{\frac{k_T}{k_H} = 0.06 \approx 1/16}$$

- (b) The analogous expression for ^{16}O and ^{18}O requires reduced masses for C^{16}O and C^{18}O bonds. These reduced masses could vary widely depending on the size of the whole molecule. I will use $^{12}\text{C}^{16}\text{O}$, for example

$$\mu_{16} = \frac{(16.0 \text{ u}) \times (12.0 \text{ u})}{(16.0 + 12.0) \text{ u}} = 6.86 \text{ u} \quad \text{and} \quad \mu_{18} = \frac{(18.0 \text{ u}) \times (12.0 \text{ u})}{(18.0 + 12.0) \text{ u}} = 7.20 \text{ u}$$

$$\lambda = \frac{(1.0546 \times 10^{-34} \text{ J s}) \times (1750 \text{ N m}^{-1})^{1/2}}{2 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}$$

$$\times \left(\frac{1}{(6.86 \text{ u})^{1/2}} - \frac{1}{(7.20 \text{ u})^{1/2}}\right) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})^{-1/2}$$

$$= 0.12 \quad \text{so} \quad \boxed{\frac{k_{18}}{k_{16}} = 0.89}$$

E25.18(b) A reaction n th-order in A has the following rate law

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

Integration yields

$$\frac{[A]^{1-n} - [A]_0^{1-n}}{1-n} = -kt$$

Let $t_{1/3}$ be the time at which $[A] = \frac{1}{3}[A]_0$, so

$$-kt_{1/3} = \frac{(\frac{1}{3}[A]_0)^{1-n} - [A]_0^{1-n}}{1-n} = \frac{[A]_0^{1-n}[(\frac{1}{3})^{1-n} - 1]}{1-n}$$

$$\text{and } t_{1/3} = \boxed{\frac{3^{n-1} - 1}{k(n-1)} [A]_0^{1-n}}$$

E25.19(b) The effective rate constant is related to the individual steps by

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a p} \quad \text{so} \quad \frac{1}{k_1} - \frac{1}{k_2} = \frac{1}{k_a} \left(\frac{1}{p_1} - \frac{1}{p_2} \right)$$

$$\begin{aligned} k_a &= \left(\frac{1}{p_1} - \frac{1}{p_2} \right) \left(\frac{1}{k_1} - \frac{1}{k_2} \right)^{-1} \\ &= \left(\frac{1}{1.09 \times 10^3 \text{ Pa}} - \frac{1}{25 \text{ Pa}} \right) \times \left(\frac{1}{1.7 \times 10^{-3} \text{ s}^{-1}} - \frac{1}{2.2 \times 10^{-4} \text{ s}^{-1}} \right)^{-1} \\ &= \boxed{9.9 \times 10^{-6} \text{ s}^{-1} \text{ Pa}^{-1}} \end{aligned}$$

E25.20(b) The equilibrium constant of the reaction is

$$K = \frac{k_f}{k_r} \quad \text{so} \quad k_f = K k_r$$

The relaxation time for the temperature jump is

$$\tau = \{k_f + k_r([B] + [C])\}^{-1} \quad \text{so} \quad k_f = \tau^{-1} - k_r([B] + [C])$$

Setting these two expressions for k_f equal yields

$$\begin{aligned} K k_r &= \tau^{-1} - k_r([B] + [C]) \quad \text{so} \quad k_r = \frac{1}{\tau(K + [B] + [C])} \\ k_r &= \frac{1}{(3.0 \times 10^{-6} \text{ s}) \times (2.0 \times 10^{-16} + 2.0 \times 10^{-4} + 2.0 \times 10^{-4}) \text{ mol L}^{-1}} \\ &= \boxed{8.3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

$$\text{and } k_f = (2.0 \times 10^{-16} \text{ mol L}^{-1}) \times (8.3 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}) = \boxed{1.7 \times 10^{-7} \text{ s}^{-1}}$$

Solutions to problems

Solutions to numerical problems

P25.2

The procedure is that described in solution to Problem 25.1. Visual inspection of the data seems to indicate that the half-life is roughly independent of the concentration. Therefore, we first try to fit the data to eqn 10*b*. As in Example 25.3 we plot $\ln\left(\frac{[A]}{[A]_0}\right)$ against time to see if a straight line is obtained. We draw up the following table (A = (CH₃)₃CBr)

t/h	0	3.15	6.20	10.00	18.30	30.80
$[A]/(10^{-2} \text{ mol L}^{-1})$	10.39	8.96	7.76	6.39	3.53	2.07
$\frac{[A]}{[A]_0}$	1	0.862	0.747	0.615	0.340	0.199
$\ln\left(\frac{[A]}{[A]_0}\right)$	0	-0.148	-0.292	-0.486	-1.080	-1.613
$\left(\frac{1}{[A]}\right)/(\text{L mol}^{-1})$	9.62	11.16	12.89	15.65	28.3	48.3

The data are plotted in Fig. 25.1. The fit to a straight line is only fair. The least squares value of k is $0.0542 \text{ h}^{-1} = 1.51 \times 10^{-5} \text{ s}^{-1}$ with a correlation coefficient of 0.996. If we try to fit the data to eqn 12*b*, which corresponds to a second-order reaction, the fit is not as good. The correlation coefficient is 0.985. Thus we conclude that the reaction is most likely **first-order**. A more complex order, which is neither first nor second, is possible, but not likely. At 43.8 h

$$\ln\left(\frac{[A]}{[A]_0}\right) = -2.359$$

$$[A] = 9.82 \times 10^{-3} \text{ mol L}^{-1}$$

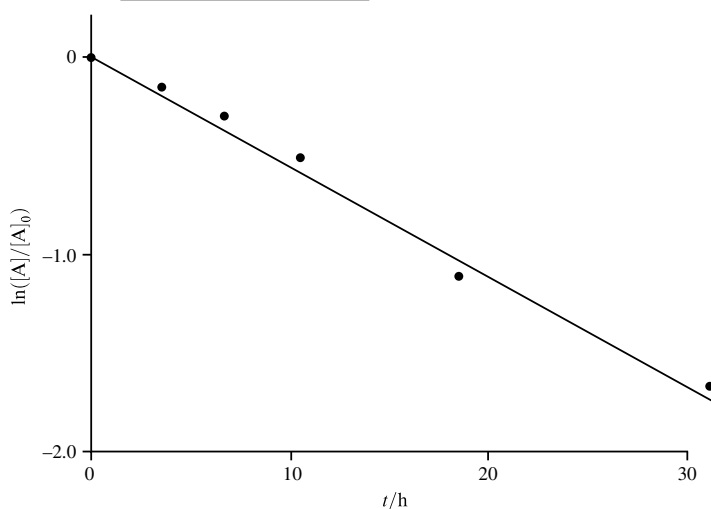


Figure 25.1

P25.4

Examination of the data shows that the half-life remains constant at about 2 minutes. Therefore, the reaction is **first-order**. This can be confirmed by fitting any two pairs of data to the integrated first-order rate law, solving for k from each pair, and checking to see that they are the same to within experimental error.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad [10b, A = \text{N}_2\text{O}_5]$$

Solving for k ,

$$k = \frac{\ln\left(\frac{[A]_0}{[A]}\right)}{t}$$

at $t = 1.00 \text{ min}$, $[A] = 0.705 \text{ mol L}^{-1}$

$$k = \frac{\ln\left(\frac{1.000}{0.705}\right)}{1.00 \text{ min}} = 0.350 \text{ min}^{-1} = 5.83 \times 10^{-3} \text{ s}^{-1}$$

at $t = 3.00 \text{ min}$, $[A] = 0.399 \text{ mol L}^{-1}$

$$k = \frac{\ln\left(\frac{1.000}{0.349}\right)}{3.00 \text{ min}} = 0.351 \text{ min}^{-1} = 5.85 \times 10^{-3} \text{ s}^{-1}$$

Values of k may be determined in a similar manner at all other times. The average value of k obtained is $5.84 \times 10^{-3} \text{ s}^{-1}$. The constancy of k , which varies only between 5.83 and $5.85 \times 10^{-3} \text{ s}^{-1}$ confirms that the reaction is **first-order**. A linear regression of $\ln[A]$ against t yields the same result.

$$t_{1/2} = \frac{\ln 2}{k} [11] = \frac{0.693}{5.84 \times 10^{-3} \text{ s}^{-1}} = 118.7 \text{ s} = \boxed{1.98 \text{ min}}$$

P25.7

$[B]_0 = \frac{1}{2}[A]_0$; hence $[A]_0 = 0.624 \text{ mol L}^{-1}$. For the reaction $2A \rightarrow B$, $[A] = [A]_0 - 2[B]$. We can therefore draw up the following table

t/s	0	600	1200	1800	2400
$[B]/(\text{mol L}^{-1})$	0	0.089	0.153	0.200	0.230
$[A]/(\text{mol L}^{-1})$	0.624	0.446	0.318	0.224	0.164

The data are plotted in Fig. 25.2(a).

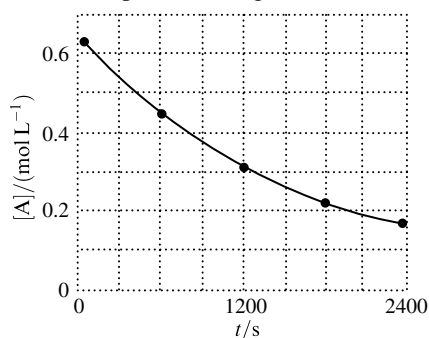


Figure 25.2(a)

We see that the half-life of A from its initial concentration is approximately 1200 s, and that its half-life from the concentration at 1200 s is also 1200 s. This indicates a first-order reaction. We confirm this conclusion by plotting the data accordingly, using

$$\ln \frac{[A]_0}{[A]} = k_A t \quad \text{if} \quad \frac{d[A]}{dt} = -k_A [A]$$

First, draw up the table

t/s	0	600	1200	1800	2400
$\ln \frac{[A]_0}{[A]}$	0	0.34	0.67	1.02	1.34

and plot the points (Fig. 25.2(b)).

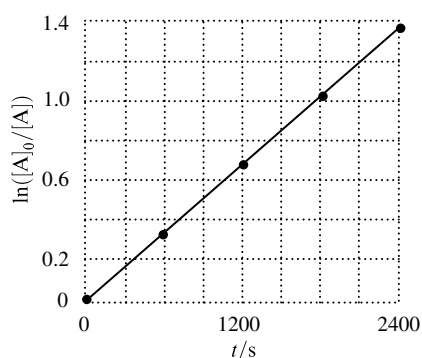


Figure 25.2(b)

The points lie as a straight line, which confirms first-order kinetics. Since the slope of the line is 5.6×10^{-4} , we conclude that $k_A = 5.6 \times 10^{-4} \text{ s}^{-1}$. To express the rate law in the form

$$v = k[A]$$

$$\text{we note that } v = -\frac{1}{2} \frac{d[A]}{dt} = -\left(\frac{1}{2}\right) \times (-k_A[A]) = \frac{1}{2}k_A[A]$$

$$\text{and hence } k = \frac{1}{2}k_A = \boxed{2.8 \times 10^{-4} \text{ s}^{-1}}$$

P25.8

The data do not extend much beyond one half-life; therefore, we cannot see whether the **half**-life is constant over the course of the reaction as a preliminary step in guessing a reaction order. In a first-order reaction, however, not only the half-life but any other similarly-defined fractional lifetime remains constant. (That is a property of the exponential function.) In this problem, we can see that the $2/3$ -life is **not** constant. (It takes less than 1.6 ms for $[\text{ClO}]$ to drop from the first recorded value ($8.49 \mu\text{mol L}^{-1}$) by more than $1/3$ of that value (to $5.79 \mu\text{mol L}^{-1}$); it takes more than 4.0 more ms for the concentration to drop by not even $1/3$ of **that** value (to $3.95 \mu\text{mol L}^{-1}$). So our working assumption is that the reaction is not first-order but second-order. Draw up the following table

t/ms	$[\text{ClO}]/(\mu\text{mol L}^{-1})$	$(1/[\text{ClO}])/(\text{L } \mu\text{mol}^{-1})$
0.12	8.49	0.118
0.62	8.09	0.124
0.96	7.10	0.141
1.60	5.79	0.173
3.20	5.20	0.192
4.00	4.77	0.210
5.75	3.95	0.253

The plot of $(1/[\text{ClO}])/(\text{L } \mu\text{mol}^{-1})$ vs. t/ms yields a good straight line; the linear least squares fit is:

$$(1/[\text{ClO}])/(\text{L } \mu\text{mol}^{-1}) = 0.118 + 0.0237(t/\text{ms}) \quad r^2 = 0.974$$

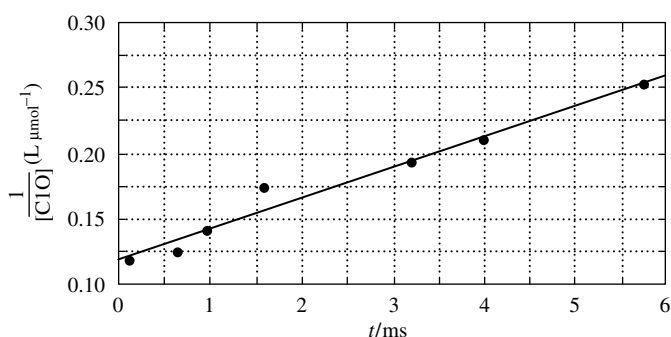


Figure 25.3

The rate constant is equal to the slope

$$k = 0.0237 \text{ L } \mu\text{mol}^{-1} \text{ ms}^{-1} = \boxed{2.37 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}}$$

The lifetime or time constant is the time required for the concentration to drop to $1/e$ of its initial value. Use the integrated second-order rate law

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

to solve for the time when $[\text{ClO}] = [\text{ClO}]_0/e$

$$\frac{e}{[\text{ClO}]_0} - \frac{1}{[\text{ClO}]_0} = kt$$

$$\text{So } t = \frac{e - 1}{k[\text{ClO}]_0} = \frac{e - 1}{(2.37 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1})(8.47 \times 10^{-6} \text{ mol L}^{-1})} = \boxed{8.56 \times 10^{-3} \text{ s}}$$

Note: $[\text{ClO}]_0$ was taken from the intercept of the best-fit equation

$$(1/[\text{ClO}]_0)/(\text{L } \mu\text{mol}^{-1}) = 0.118 \quad \text{so} \quad [\text{ClO}]_0 = 8.47 \mu\text{mol L}^{-1}$$

P25.11 Using spreadsheet software to evaluate eqn 25.36, one can draw up a plot like the following. The curves in this plot represent the concentration of the intermediate [I] as a function of time. They are labeled with the ratio k_1/k_2 , where $k_2 = 1 \text{ s}^{-1}$ for all curves and k_1 varies. The thickest curve, labeled 10, corresponds to $k_1 = 10 \text{ s}^{-1}$, as specified in part a of the problem. As the ratio k_1/k_2 gets smaller (or, as the problem puts it, the ratio k_2/k_1 gets larger), the concentration profile for I becomes lower, broader, and flatter; that is, [I] becomes more nearly constant over a longer period of time. This is the nature of the steady-state approximation, which becomes more and more valid as consumption of the intermediate becomes fast compared with its formation.

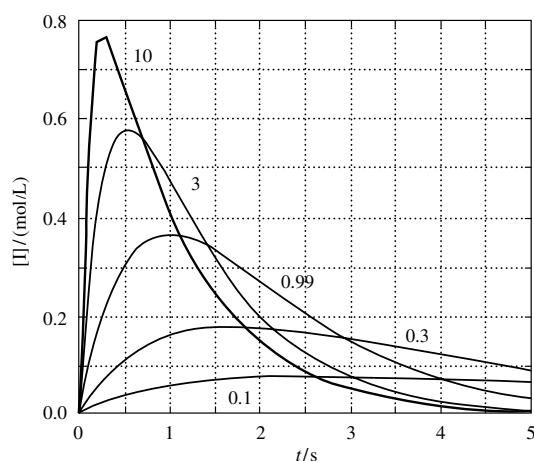


Figure 25.4

P25.13
$$E_a = \frac{R \ln \left(\frac{k'_{\text{eff}}}{k_{\text{eff}}} \right)}{\left(\frac{1}{T} - \frac{1}{T'} \right)} \text{ [Exercise 25.16(a) from eqn 25.25]} = \frac{R \ln 3}{\frac{1}{343 \text{ K}} - \frac{1}{292 \text{ K}}} = \boxed{-18 \text{ kJ mol}^{-1}}$$

But $k_{\text{eff}} = k K_1 K_2$ [Problem 25.12]

$$\ln k_{\text{eff}} = \ln k + \ln K_1 + \ln K_2$$

$$E_a = -R \frac{d \ln k_{\text{eff}}}{d(1/T)} \text{ [25.26]} = E'_a + \Delta_r H_1 + \Delta_r H_2$$

since $\frac{d \ln K}{d(1/T)} = \frac{-\Delta_r H}{R}$ [van't Hoff equation, Chapter 9] Therefore,

$$E'_a = E_a - \Delta_r H_1 - \Delta_r H_2 = [-(18) + (14) + (14)] \text{ kJ mol}^{-1} = \boxed{+10 \text{ kJ mol}^{-1}}$$

P25.15
$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a [A]} \text{ [25.63]}$$

or, in terms of pressure of A

$$\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a p}$$

and we expect a straight line when $\frac{1}{k}$ is plotted against $\frac{1}{p}$. We draw up the following table

p/Torr	84.1	11.0	2.89	0.569	0.120	0.067
$1/(p/\text{Torr})$	0.012	0.091	0.346	1.76	8.33	14.9
$10^{-4}/(k/s^{-1})$	0.336	0.448	0.629	1.17	2.55	3.30

These points are plotted in Fig. 25.5. There are marked deviations at low pressures, indicating that the Lindemann theory is deficient in that region.

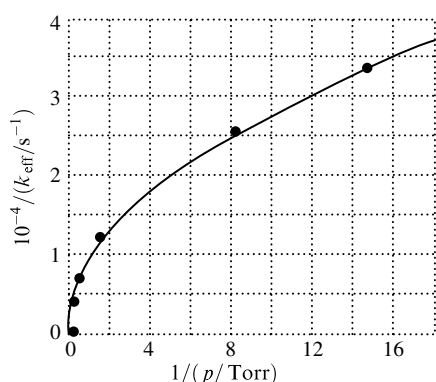


Figure 25.5

Solutions to theoretical problems

P25.18 We assume a pre-equilibrium (as the initial step is fast), and write

$$K = \frac{[A]^2}{[A_2]}, \quad \text{implying that} \quad [A] = K^{1/2}[A_2]^{1/2}$$

The rate-determining step then gives

$$v = \frac{d[P]}{dt} = k_2[A][B] = \boxed{k_2 K^{1/2}[A_2]^{1/2}[B]} = k_{\text{eff}}[A_2]^{1/2}[B]$$

where $k_{\text{eff}} = k_2 K^{1/2}$.

P25.20

$$\frac{d[P]}{dt} = k[A][B]$$

Let the initial concentrations be A_0 , B_0 , and $[P]_0 = 0$. Then, when an amount x of P is formed, the amount of A changes to $A_0 - 2x$ and that of B changes to $B_0 - 3x$. Therefore

$$\frac{d[P]}{dt} = \frac{dx}{dt} = k(A_0 - 2x)(B_0 - 3x) \quad \text{with } x = 0 \text{ at } t = 0.$$

$$\begin{aligned} \int_0^t k \, dt &= \int_0^x \frac{dx}{(A_0 - 2x) \times (B_0 - 3x)} \\ &= \int_0^x \left(\frac{6}{2B_0 - 3A_0} \right) \times \left(\frac{1}{3(A_0 - 2x)} - \frac{1}{2(B_0 - 3x)} \right) dx \\ &= \left(\frac{-1}{(2B_0 - 3A_0)} \right) \times \left(\int_0^x \frac{dx}{x - (1/2)A_0} - \int_0^x \frac{dx}{x - (1/3)B_0} \right) \end{aligned}$$

$$kt = \left(\frac{-1}{(2B_0 - 3A_0)} \right) \times \left[\ln \left(\frac{x - \frac{1}{2}A_0}{-\frac{1}{2}A_0} \right) - \ln \left(\frac{x - \frac{1}{3}B_0}{-\frac{1}{3}B_0} \right) \right]$$

$$= \left(\frac{-1}{(2B_0 - 3A_0)} \right) \ln \left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)} \right)$$

$$= \boxed{\left(\frac{1}{(3A_0 - 2B_0)} \right) \ln \left(\frac{(2x - A_0)B_0}{A_0(3x - B_0)} \right)}$$

P25.23 $kt = \left(\frac{1}{n-1}\right) \times \left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right)$ [Exercise 25.18(a), $n \neq 1$]

At $t = t_{1/2}$, $kt_{1/2} = \left(\frac{1}{n-1}\right) \left[\left(\frac{2}{A_0}\right)^{n-1} - \left(\frac{1}{A_0}\right)^{n-1}\right]$

At $t = t_{3/4}$, $[A] = \frac{3}{4}[A]_0$

$$kt_{3/4} = \left(\frac{1}{n-1}\right) \left[\left(\frac{4}{3A_0}\right)^{n-1} - \left(\frac{1}{A_0}\right)^{n-1}\right]$$

Hence, $\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1} - 1}{\left(\frac{4}{3}\right)^{n-1} - 1}$

P25.24 Let the forward rates be written as

$$r_1 = k_1[A], \quad r_2 = k_2[B], \quad r_3 = k_3[C]$$

and the reverse rates as

$$r'_1 = k'_1[B], \quad r'_2 = k'_2[C], \quad r'_3 = k'_3[D]$$

The net rates are then

$$R_1 = k_1[A] - k'_1[B], \quad R_2 = k_2[B] - k'_2[C], \quad R_3 = k_3[C] - k'_3[D]$$

But $[A] = [A]_0$ and $[D] = 0$, so that the steady-state equations for the rates of the intermediates are

$$k_1[A]_0 - k'_1[B] = k_2[B] - k'_2[C] = k_3[C]$$

From the second of these equations we find

$$[C] = \frac{k_2[B]}{k'_2 + k_3}$$

After inserting this expression for $[C]$ into the first of the steady-state equations we obtain

$$[B] = [A]_0 \times \frac{k_1}{k_2 + k'_1 - \left(\frac{k'_2 k_2}{k'_2 + k_3}\right)}$$

Thus, at the steady state

$$R_1 = R_2 = R_3 = [A]_0 k_1 \times \left(1 - \frac{k'_1}{k_2 + k'_1 - \left(\frac{k'_2 k_2}{k'_2 + k_3}\right)}\right)$$

P25.25

$$v = k([A]_0 - x)([B]_0 + x)$$

$$\frac{dv}{dx} = k([A]_0 - x) - k([B]_0 + x)$$

The extrema correspond to $\frac{dv}{dx} = 0$, or

$$[A]_0 - x = [B]_0 + x \quad \text{or} \quad 2x = [A]_0 - [B]_0 \quad \text{or} \quad x = \frac{[A]_0 - [B]_0}{2}$$

Substitute into v to obtain

$$v_{\max} = k \left(\frac{[A]_0}{2} + \frac{[B]_0}{2} \right) \times \left(\frac{[B]_0}{2} + \frac{[A]_0}{2} \right) = k \left(\frac{[A]_0 + [B]_0}{2} \right)^2$$

Since v and x cannot be negative in the reaction,

$$\boxed{[B]_0 \leq [A]_0}$$

To see the variation of v with x , let $[B]_0 = [A]_0$. The rate equation becomes

$$v = k([A]_0 - x)([A]_0 + x) = k([A]_0^2 - x^2) = k[A]_0^2 - kx^2$$

$$\text{or } \frac{v}{k[A]_0^2} = \left(1 - \frac{x^2}{[A]_0^2} \right) = \left(1 + \frac{x}{[A]_0} \right) \left(1 - \frac{x}{[A]_0} \right)$$

Thus we plot $\frac{v}{k[A]_0^2}$ against $\left(1 - \frac{x^2}{[A]_0^2} \right)$ from $\frac{x}{[A]_0} = 0$

The plot is shown in Fig. 25.6 in which $X = \frac{x}{[A]_0}$. $\frac{x}{[A]_0} \leq 1$ corresponds to reality

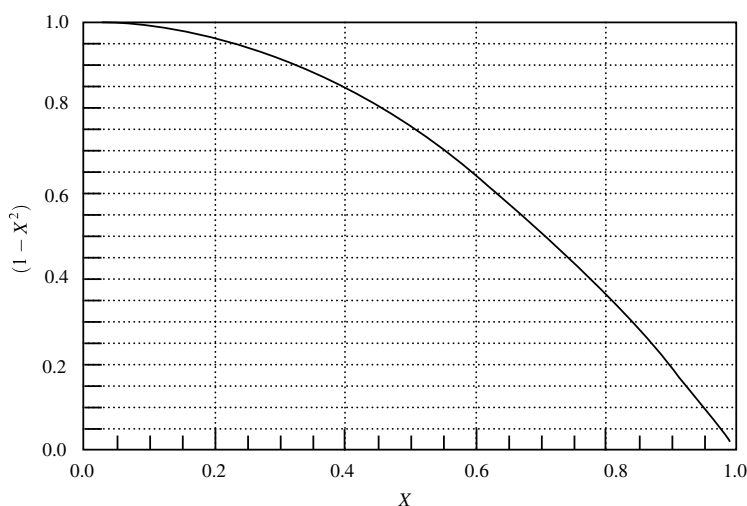


Figure 25.6

P25.26 For $A \rightarrow B \rightarrow C$

$$[I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) [A]_0 \quad [25.36]$$

$$\frac{d[I]}{dt} = \frac{k_a}{k_b - k_a} (k_b e^{-k_b t} - k_a e^{-k_a t})$$

$[I]$ reaches a maximum when $d[I]/dt=0$. This occurs when t satisfies the equation

$$k_b e^{-k_b t_{\max}} - k_a e^{-k_a t_{\max}} = 0$$

$$k_b e^{-k_b t_{\max}} \left(1 - \frac{k_a e^{-(k_a - k_b) t_{\max}}}{k_b} \right) = 0$$

$$1 - \frac{k_a}{k_b} e^{-(k_a - k_b) t_{\max}} = 0$$

$$e^{-(k_a - k_b) t_{\max}} = k_b / k_a$$

$$-(k_a - k_b) t_{\max} = \ln(k_b / k_a)$$

$$t_{\max} = \frac{\ln(k_b / k_a)}{(k_b - k_a)} = \frac{(k_a / k_b) \ln(k_a / k_b)}{k_a \left(\frac{k_a}{k_b} - 1 \right)}$$

For $k_a = 1.0 \text{ min}^{-1}$, the times at which $[I]$ is a maximum are

k_a / k_b	5	1	0.5
t_{\max} / min	2.01	1	0.693

The evaluation for t_{\max} when $k_a / k_b = 1$ requires special care. Imagine $k_a / k_b > 0$ and take $\lim_{k_a / k_b \rightarrow 1} (t_{\max})$. In this limit the value of $\left(\frac{k_a}{k_b} - 1 \right)$ in the denominator becomes very small (call this value x) and can be viewed as being part of the Taylor series expansion of $\ln(1 + x)$

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} + \dots \approx x$$

$$\begin{aligned} \lim_{k_a / k_b \rightarrow 1} (t_{\max}) &= \frac{1}{k_a} \lim_{k_a / k_b \rightarrow 1} \left\{ \frac{(k_a / k_b) \ln(k_a / k_b)}{\ln(k_a / k_b)} \right\} \\ &= \frac{1}{k_a} \end{aligned}$$

Plots of $\frac{[I]}{[A]_0}$ for $k_a / k_b = 5, 1$, and 0.5 are shown in Fig. 25.6.

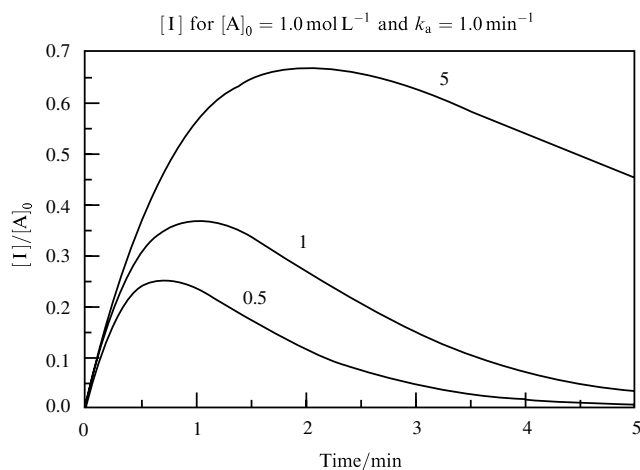


Figure 25.6(a)

For $A + B \rightarrow P$

$$v = \frac{dx}{dt} = k[A][B] = k([A]_0 - x)([B]_0 - x)$$

$$\int_{x=0}^x \frac{dx}{([A]_0 - x)([B]_0 - x)} = \int_{t=0}^t k dt = kt$$

$$\int_{x=0}^x \frac{dx}{[A]_0[B]_0 - ([A]_0 + [B]_0)x + x^2} = kt$$

The integral on the left may be found in standard mathematics handbooks.

$$\int \frac{dz}{az^2 + bz + c} = \frac{1}{\sqrt{b^2 - 4ac}} \ln \left(\frac{2ax + b - \sqrt{b^2 - 4ac}}{2ax + b + \sqrt{b^2 - 4ac}} \right)$$

The transformations to our working equation are

$$\begin{aligned} a &\rightarrow 1 & b &\rightarrow -([A]_0 + [B]_0) \\ c &\rightarrow [A]_0[B]_0 & \sqrt{b^2 - 4ac} &\rightarrow [A]_0 - [B]_0 \\ b - \sqrt{b^2 - 4ac} &\rightarrow -2[A]_0 \\ b + \sqrt{b^2 - 4ac} &\rightarrow -2[B]_0 \end{aligned}$$

$$\frac{1}{[A]_0 - [B]_0} \ln \left(\frac{x - [A]_0}{x - [B]_0} \right) \Bigg|_{x=0}^x = kt$$

$$\frac{1}{[A]_0 - [B]_0} \left\{ \ln \left(\frac{[A]_0 - x}{[B]_0 - x} \right) - \ln \left(\frac{[A]_0}{[B]_0} \right) \right\} = kt$$

$$\frac{1}{[A]_0 - [B]_0} \ln \left(\frac{[B]_0([A]_0 - x)}{[A]_0([B]_0 - x)} \right) = kt$$

This can also be written in the form

$$\boxed{\frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[A]_0([B]_0 - x)}{[B]_0([A]_0 - x)} \right) = kt}$$

We will now solve this for x

$$\frac{[B]_0 - x}{[A]_0 - x} = \frac{[B]_0}{[A]_0} e^{-\{([A]_0 - [B]_0)kt\}} \equiv f(t)$$

$$[B]_0 - x = [A]_0 f(t) - f(t)x$$

$$(1 - f(t))x = [B]_0 - [A]_0 f(t)$$

$$x = \frac{[B]_0 - [A]_0 f(t)}{1 - f(t)} = \frac{[B]_0 - [B]_0 e^{-\{([A]_0 - [B]_0)kt\}}}{1 - ([B]_0/[A]_0) e^{-\{([A]_0 - [B]_0)kt\}}}$$

Solutions to applications

P25.28 The first-order half-life is related to the rate constant by

$$t_{1/2} = \frac{\ln 2}{k} \quad \text{so} \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{28.1 \text{ y}} = 2.47 \times 10^{-2} \text{ y}^{-1}$$

The integrated rate law tells us

$$[{}^{90}\text{Sr}] = [{}^{90}\text{Sr}]_0 e^{-kt} \quad \text{so} \quad m = m_0 e^{-kt}$$

where m is the mass of ${}^{90}\text{Sr}$.

(a) After 18 y: $m = (1.00 \mu\text{g}) \times \exp[-(2.47 \times 10^{-2} \text{ y}^{-1}) \times (18 \text{ y})] = \boxed{0.642 \mu\text{g}}$

(b) After 70 y: $m = (1.00 \mu\text{g}) \times \exp[-(2.47 \times 10^{-2} \text{ y}^{-1}) \times (70 \text{ y})] = \boxed{0.177 \mu\text{g}}$

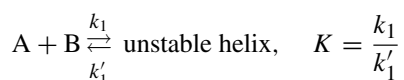
P25.30 We assume a pre-equilibrium (as the initial step is fast), and write

$$K = \frac{[\text{unstable helix}]}{[A][B]}, \quad \text{implying that} \quad [\text{unstable helix}] = K[A][B]$$

The rate-determining step then gives

$$v = \frac{d[\text{double helix}]}{dt} = k_2[\text{unstable helix}] = k_2 K[A][B] = \boxed{k[A][B]} \quad [k = k_2 K]$$

The equilibrium constant is the outcome of the two processes



Therefore, with $v = k[A][B]$, $\boxed{k = \frac{k_1 k_2}{k'_1}}$

P25.33 (a) The rate of reaction is

$$v = k[\text{CH}_4][\text{OH}]$$

$$= (1.13 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{-14.1 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (263 \text{ K})}\right)$$

$$\times (4.0 \times 10^{-8} \text{ mol L}^{-1}) \times (1.5 \times 10^{-15} \text{ mol L}^{-1}) = \boxed{1.1 \times 10^{-16} \text{ mol L}^{-1} \text{ s}^{-1}}$$

- (b) The mass is the amount consumed (in moles) times the molar mass; the amount consumed is the rate of consumption times the volume of the “reaction vessel” times the time

$$\begin{aligned} m &= MvVt = (0.01604 \text{ kg mol}^{-1}) \times (1.1 \times 10^{-16} \text{ mol L}^{-1} \text{ s}^{-1}) \\ &\quad \times (4 \times 10^{21} \text{ L}) \times (365 \times 24 \times 3600 \text{ s}) \\ &= \boxed{2.2 \times 10^{11} \text{ kg or 220 Tg}} \end{aligned}$$

P25.35 The initial rate is

$$\begin{aligned} v_0 &= (3.6 \times 10^6 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}) \times (5 \times 10^{-4} \text{ mol L}^{-1})^2 \times (10^{-4.5} \text{ mol L}^{-1})^2 \\ &= \boxed{9 \times 10^{-10} \text{ mol L}^{-1} \text{ s}^{-1}} \end{aligned}$$

The half-life for a second-order reaction is

$$t_{1/2} = \frac{1}{k'[\text{HSO}_3^-]_0}$$

where k' is the rate constant in the expression

$$-\frac{d[\text{HSO}_3^-]}{dt} = k'[\text{HSO}_3^-]^2$$

Comparison to the given rate law and rate constant shows

$$\begin{aligned} k' &= 2k[\text{H}^+]^2 = 2(3.6 \times 10^6 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}) \times (10^{-4.5} \text{ mol L}^{-1})^2 \\ &= 7.2 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\text{and } t_{1/2} = \frac{1}{(7.2 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}) \times (5 \times 10^{-4} \text{ mol L}^{-1})} = \boxed{2.8 \times 10^5 \text{ s} = 3 \text{ days}}$$