22 The rates of chemical reactions

Answers to discussion questions

D22.2 No solution.

D22.4 The overall reaction order is the sum of the powers of the concentrations of all of the substances appearing in the *experimental* rate law for the reaction (eqn 22.7); hence, it is the sum of the individual orders (exponents) associated with a given reactant (or product). Reaction order is an experimentally determined, *not theoretical*, quantity, although theory may attempt to predict it. *Molecularity* is the number of reactant molecules participating in an elementary reaction. This concept has meaning only for an elementary reaction, but reaction order applies to any reaction. In general, reaction order bears no necessary relation to the stoichiometry of the reaction, with the exception of elementary reactions, where the order of the reaction corresponds to the number of molecules participating in the reaction; that is, to its molecularity. Thus for an elementary reaction, overall order and molecularity are the same and are determined by the stoichiometry.

D22.6 The steady-state approximation is the assumption that the rate of change of the concentrations of intermediates in consecutive chemical reactions is negligibly small. It is a good approximation when at least one of the reaction steps involving the intermediate is very fast, that is, has a large rate constant relative to other steps. See Section 22.7(b). A pre-equilibrium approximation is similar in that it is a good approximation when the rate of formation of the intermediate from the reactants and the rate of its reversible decay back to the reactions are both very fast in comparison to the rate of formation of the product from the intermediate. This results in the intermediate being in approximate equilibrium with the reactants over relatively long time periods (though short compared to the overall time scale of the reaction). Hence the concentration of the intermediate remains approximately constant over the time period that the equilibrium can be considered to be maintained. This allows one to relate the rate constants and concentrations to each other through a constant (the pre-equilibrium constant). See Section 22.7(e).

D22.8 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

$$E_a = RT^2\left(\frac{\mathrm{d}\ln k}{\mathrm{d}T}\right) \quad [22.30]$$

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 behavior is sometimes a sign that quantum mechanical tunnelling is playing a significant role in the reaction.

D22.10 The expression $k = k_a k_b[\mathrm{A}]/(k_b + k'_a[\mathrm{A}])$ for the effective rate constant of a unimolecular reaction $\mathrm{A} \rightarrow \mathrm{P}$ is based on the validity of the assumption of the existence of the pre-equilibrium $\mathrm{A}+\mathrm{A} \underset{k'_a}{\overset{k_a}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{A}$. 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

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

Hence, a test of the theory is to plot $1/k$ against $1/[\mathrm{A}]$, 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 $1/[\mathrm{A}]$ has a pronounced curvature, corresponding to a larger value of k (a smaller value of $1/k$) at high pressures (low $1/[\mathrm{A}]$) than would be expected by extrapolation of the reasonably linear low pressure (high $1/[\mathrm{A}]$) data.

Solutions to exercises

E22.1(b) $$v = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{1}{3}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = 1.00\,\mathrm{mol\,dm^{-3}\,s^{-1}}, \text{ so}$$

Rate of consumption of A = $\boxed{1.0\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

Rate of consumption of B = $\boxed{3.0\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

Rate of formation of C = $\boxed{1.0\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

Rate of formation of D = $\boxed{2.0\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

E22.2(b) Rate of consumption of B = $-\dfrac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \boxed{1.00\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

Rate of reaction = $-\dfrac{1}{3}\dfrac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \boxed{0.33\ \mathrm{mol\ dm^{-3}\ s^{-1}}} = \dfrac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = \dfrac{1}{2}\dfrac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = -\dfrac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}$

Rate of formation of C = $\boxed{0.33\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

Rate of formation of D = $\boxed{0.66\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

Rate of consumption of A = $\boxed{0.33\ \mathrm{mol\ dm^{-3}\ s^{-1}}}$

E22.3(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, dm, s units, the units of k are $\boxed{\text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}}$

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

(b) $v = \dfrac{\text{d[C]}}{\text{d}t}$ so $\boxed{\dfrac{\text{d[C]}}{\text{d}t} = -k[\text{A}][\text{B}]^2}$

E22.4(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 $\boxed{\text{s}^{-1}}$

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

E22.5(b) The rate law is

$$v = k[\text{A}]^a \propto p^a = \{p_0(1-f)\}^a$$

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

$$\frac{v_1}{v_2} = \frac{\{p_0(1-f_1)\}^a}{\{p_0(1-f_2)\}^a} = \left(\frac{1-f_1}{1-f_2}\right)^a \quad \text{and} \quad a = \frac{\ln(v_1/v_2)}{\ln\left(\dfrac{1-f_1}{1-f_2}\right)} = \frac{\ln(9.71/7.67)}{\ln\left(\dfrac{1-0.100}{1-0.200}\right)} = \boxed{2.00}$$

E22.6(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 22.3. 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 $\boxed{0}$.

E22.7(b) The rate law is

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

The half-life formula in eqn 22.13 is based on the assumption that

$$-\frac{d[A]}{dt} = k[A].$$

That is, it would be accurate to take the half-life from the table and say

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

where $k' = 2k$. Thus

$$t_{1/2} = \frac{\ln 2}{2(2.78 \times 10^{-7}\,\mathrm{s}^{-1})} = \boxed{1.80 \times 10^{6}\,\mathrm{s}}$$

Likewise, we modify the integrated rate law (eqn 22.12b), noting that pressure is proportional to concentration:

$$p = p_0 e^{-2kt}$$

(a) Therefore, after 10 h, we have

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

(b) After 50 h,

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

E22.8(b) From Table 22.3, we see that for $A + 2B \rightarrow P$ the integrated rate law is

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

(a) Substituting the data after solving for k

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

$$= \boxed{3.4\overline{7} \times 10^{-3}\mathrm{dm^3 mol^{-1} s^{-1}}}$$

(b) The half-life in terms of A is the time when $[A] = [A]_0/2 = [P]$, so

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

which reduces to

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

$$= \frac{1}{(3.4\overline{7} \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times (-0.070\,\mathrm{mol\,dm^{-3}})} \times \ln\left(2 - \frac{0.150}{0.080}\right)$$

$$= 856\overline{1}\,\mathrm{s} = \boxed{2.4\,\mathrm{h}}$$

The half-life in terms of B is the time when $[B] = [B]_0/2$ and $[P] = [B]_0/4$:

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

which reduces to

$$\begin{aligned} t_{1/2}(B) &= \frac{1}{k([B]_0 - 2[A]_0)} \ln \left(\frac{[A]_0/2}{[A]_0 - [B]_0/4} \right) \\ &= \frac{1}{(3.4\overline{7} \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times (-0.070\,\mathrm{mol\,dm^{-3}})} \times \ln \left(\frac{0.075/2}{0.075 - (0.080/4)} \right) \\ &= 15\overline{76}\,\mathrm{s} = \boxed{0.44\ \mathrm{h}} \end{aligned}$$

E22.9(b) (a) The dimensions of a second-order constant are

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

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

The dimensions of a third-order rate constant are

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

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

COMMENT. Technically, "molecule" is not a unit, so a number of molecules is simply a number of individual objects, that is, a pure number. In the chemical kinetics literature, it is common to see rate constants given in molecular units reported in units of $\mathrm{m^3\ s^{-1}}$, $\mathrm{m^6\ s^{-1}}$, $\mathrm{cm^3\ s^{-1}}$, etc.

(b) 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 $\mathrm{N\,m^{-2}} = \mathrm{Pa}$, so the units of k are $\boxed{\mathrm{Pa^{-1}\ s^{-1}}}$

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 pressure units, the units of k are $\boxed{\mathrm{Pa^{-2}\ s^{-1}}}$.

E22.10(b) The integrated rate law is

$$kt = \frac{1}{[B]_0 - 2[A]_0} \ln \frac{[A]_0([B]_0 - 2[C])}{([A]_0 - [C])[B]_0} \quad \text{[Table 22.3]}$$

Solving for [C] yields, after some rearranging

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

$$\text{so} \quad \frac{[\mathrm{C}]}{\mathrm{mol\,dm^{-3}}} = \frac{(0.025) \times (0.150) \times (\mathrm{e}^{0.21\times(0.100)\times t/\mathrm{s}} - 1)}{(0.150) \times \mathrm{e}^{0.21\times(0.100)\times t/\mathrm{s}} - 2 \times (0.025)} = \frac{(3.7\bar{5} \times 10^{-3}) \times (\mathrm{e}^{0.021\times t/\mathrm{s}} - 1)}{(0.150) \times \mathrm{e}^{0.021\times t/\mathrm{s}} - (0.050)}$$

(a) $$[\mathrm{C}] = \frac{(3.7\bar{5} \times 10^{-3}) \times (\mathrm{e}^{0.21} - 1)}{(0.150) \times \mathrm{e}^{0.21} - (0.050)}\ \mathrm{mol\,dm^{-3}} = \boxed{6.5 \times 10^{-3}\ \mathrm{mol\,dm^{-3}}}$$

(b) $$[\mathrm{C}] = \frac{(3.7\bar{5} \times 10^{-3}) \times (\mathrm{e}^{12.6} - 1)}{(0.150) \times \mathrm{e}^{12.6} - (0.050)}\ \mathrm{mol\,dm^{-3}} = \boxed{0.025\ \mathrm{mol\,dm^{-3}}}$$

E22.11(b) The rate law is

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

which integrates to

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

$$t = \left(\frac{1}{4(3.50 \times 10^{-4}\ \mathrm{dm^6\,mol^{-2}\,s^{-1}})}\right) \times \left(\frac{1}{(0.021\ \mathrm{mol\,dm^{-3}})^2} - \frac{1}{(0.077\ \mathrm{mol\,dm^{-3}})^2}\right)$$

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

E22.12(b) A reaction nth-order in A has the following rate law

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

Integration yields

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

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

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

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

E22.13(b) The equilibrium constant of the reaction is the ratio of rate constants of the forward and reverse reactions:

$$K = \frac{k_\mathrm{f}}{k_\mathrm{r}} \quad \text{so} \quad k_\mathrm{f} = Kk_\mathrm{r}.$$

The relaxation time for the temperature jump is (Example 22.4):

$$\tau = \{k_\mathrm{f} + k_\mathrm{r}([\mathrm{B}] + [\mathrm{C}])\}^{-1} \quad \text{so} \quad k_\mathrm{f} = \tau^{-1} - k_\mathrm{r}([\mathrm{B}] + [\mathrm{C}])$$

Setting these two expressions for $k_{\rm f}$ equal yields

$$Kk_{\rm r} = \tau^{-1} - k_{\rm r}([\mathrm{B}] + [\mathrm{C}]) \quad \text{so} \quad k_{\rm r} = \frac{1}{\tau(K + [\mathrm{B}] + [\mathrm{C}])}$$

Hence

$$k_{\rm r} = \frac{1}{(3.0 \times 10^{-6}\,\mathrm{s}) \times (2.0 \times 10^{-16} + 2.0 \times 10^{-4} + 2.0 \times 10^{-4})\,\mathrm{mol\,dm^{-3}}}$$
$$= \boxed{8.3 \times 10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

and $k_{\rm f} = (2.0 \times 10^{-16}\,\mathrm{mol\,dm^{-3}}) \times (8.3 \times 10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}) = \boxed{1.7 \times 10^{-7}\mathrm{s}^{-1}}$

E22.14(b) The rate constant is given by

$$k = A\exp\left(\frac{-E_{\rm a}}{RT}\right) \quad [22.31]$$

so at 24 °C it is

$$1.70 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}} = A\exp\left(\frac{-E_{\rm a}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times [(24 + 273)\,\mathrm{K}]}\right)$$

and at 37 °C it is

$$2.01 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}} = A\exp\left(\frac{-E_{\rm a}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times [(37 + 273)\,\mathrm{K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} = \exp\left[\left(\frac{-E_{\rm a}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times \left(\frac{1}{297\,\mathrm{K}} - \frac{1}{310\,\mathrm{K}}\right)\right]$$

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

$$\text{and } E_{\rm a} = -\left(\frac{1}{297\,\mathrm{K}} - \frac{1}{310\,\mathrm{K}}\right)^{-1}\ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})$$
$$= 9.9 \times 10^{3}\,\mathrm{J\,mol^{-1}} = \boxed{9.9\,\mathrm{kJ\,mol^{-1}}}$$

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

$$A = k\exp\left(\frac{E_{\rm a}}{RT}\right) = (1.70 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}) \times \exp\left(\frac{9.9 \times 10^{3}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (297\,\mathrm{K})}\right)$$
$$= \boxed{0.94\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

E22.15(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

$$\frac{k_{\rm T}}{k_{\rm H}} = \mathrm{e}^{-\lambda}, \text{ where } \lambda = \left(\frac{\hbar k_{\rm f}^{1/2}}{2k_{\rm B}T}\right) \times \left(\frac{1}{\mu_{\rm CH}^{1/2}} - \frac{1}{\mu_{\rm CD}^{1/2}}\right) \quad [22.53 \text{ with } hc\tilde{\nu} = \hbar\omega = \hbar(k/\mu)^{1/2}]$$

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

$$\lambda \approx \frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(450\,\mathrm{N\,m^{-1}})^{1/2}}{2\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}$$

$$\times\left(\frac{1}{(1\,\mathrm{u})^{1/2}}-\frac{1}{(3\,\mathrm{u})^{1/2}}\right)\times(1.66\times10^{-27}\,\mathrm{kg\,u^{-1}})^{-1/2}$$

$$\approx 2.8$$

so $\dfrac{k_\mathrm{T}}{k_\mathrm{H}} \approx \mathrm{e}^{-2.8} = \boxed{0.06 \approx 1/16}$

(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 rather widely depending on the size of the whole molecule, but in no case will they be terribly different for the two isotopes. Take ^{12}CO, for example:

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

$$\lambda = \frac{(1.0546\times10^{-34}\,\mathrm{J\,s})\times(1750\,\mathrm{N\,m^{-1}})^{1/2}}{2\times(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}$$

$$\times\left(\frac{1}{(6.86\,\mathrm{u})^{1/2}}-\frac{1}{(7.20\,\mathrm{u})^{1/2}}\right)\times(1.66\times10^{-27}\,\mathrm{kg\,u^{-1}})^{-1/2}$$

$$= 0.12$$

so $\dfrac{k_{18}}{k_{16}} = \mathrm{e}^{-0.12} = \boxed{0.89}$

At the other extreme, the O atoms could be attached to heavy fragments such that the effective mass of the relevant vibration approximates the mass of the oxygen isotope. That is, $\mu_{16} \approx 16\,\mathrm{u}$ and $\mu_{18} \approx 18\,\mathrm{u}$

so $\lambda \approx 0.19$ so $\dfrac{k_{18}}{k_{16}} = \mathrm{e}^{-0.19} = \boxed{0.83}$

E22.16(b) $\dfrac{1}{k} = \dfrac{k_\mathrm{a}'}{k_\mathrm{a}k_\mathrm{b}} + \dfrac{1}{k_\mathrm{a}p_\mathrm{A}}$ [analogous to 22.67]

Therefore, for two different pressures we have

$$\frac{1}{k}-\frac{1}{k'} = \frac{1}{k_\mathrm{a}}\left(\frac{1}{p}-\frac{1}{p'}\right),$$

so $k_\mathrm{a} = \left(\dfrac{1}{p}-\dfrac{1}{p'}\right)\left(\dfrac{1}{k}-\dfrac{1}{k'}\right)^{-1}$

$$= \left(\frac{1}{1.09\times10^{3}\,\mathrm{Pa}}-\frac{1}{25\,\mathrm{Pa}}\right)\times\left(\frac{1}{1.7\times10^{-3}\,\mathrm{s^{-1}}}-\frac{1}{2.2\times10^{-4}\,\mathrm{s^{-1}}}\right)^{-1}$$

$$= \boxed{9.9\times10^{-6}\mathrm{s^{-1}Pa^{-1}}} = \boxed{9.9\,\mathrm{s^{-1}MPa^{-1}}}$$

Solutions to problems

Solutions to numerical problems

P22.2 The procedure is that described in solution to Problem 22.1. 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 22.12b:

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

As in Example 22.3 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 = $(CH_3)_3CBr$)

t/h	0	3.15	6.20	10.00	18.30	30.80
$[A]/(10^{-2}\,mol\,dm^{-3})$	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
$\left(\frac{1}{[A]}\right)\Big/(dm^3\,mol^{-1})$	9.62	11.16	12.89	15.65	28.3	48.3

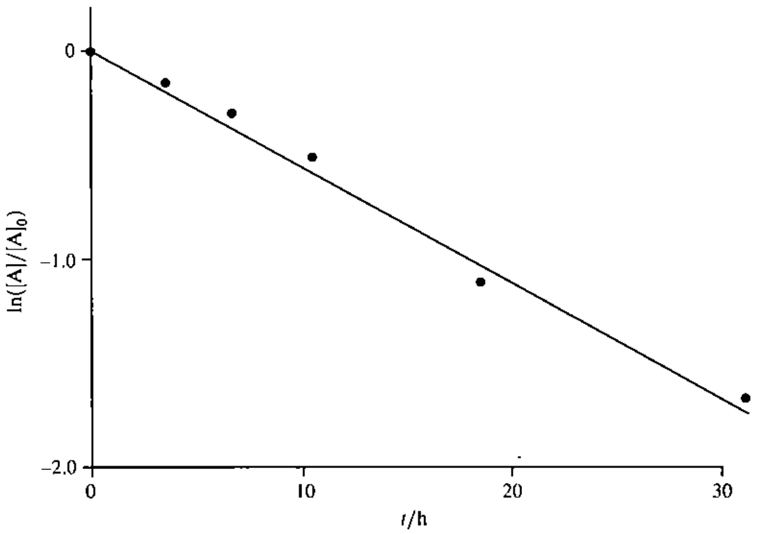


Figure 22.1

The data are plotted in Figure 22.1. The fit to a straight line is only fair, but the deviations look more like experimental scatter than systematic curvature. The correlation coefficient is 0.996. If we try to fit the data to eqn 22.15b, which corresponds to a second-order reaction, the fit is not as good; that correlation coefficient is 0.985. Thus we conclude that the reaction is most likely $\boxed{\text{first-order}}$. A non-integer order, neither first nor second, is also possible.

The rate constant k is the negative of the slope of the first-order plot:

$$k = 0.0542\,\mathrm{h}^{-1} = \boxed{1.51 \times 10^{-5}\mathrm{s}^{-1}}$$

At 43.8 h

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -(0.0542\,\mathrm{h}^{-1}) \times (43.8\,\mathrm{h}) = -2.359$$

$$[\mathrm{A}] = (10.39 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}) \times \mathrm{e}^{-2.359} = \boxed{9.82 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}}$$

P22.4 Examination of the data shows that the half-life remains constant at about 2 minutes. Therefore, the reaction is $\boxed{\text{first-order}}$. 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.

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt\ [22.12\mathrm{b}, \mathrm{A} = \mathrm{N_2O_5}]$$

Solving for k,

$$k = \frac{\ln([\mathrm{A}]_0/[\mathrm{A}])}{t}$$

At $t = 1.00$ min, $[\mathrm{A}] = 0.705\,\mathrm{mol\,dm^{-3}}$ and

$$k = \frac{\ln(1.000/0.705)}{1.00\,\mathrm{min}} = 0.350\,\mathrm{min}^{-1} = 5.83 \times 10^{-3}\,\mathrm{s}^{-1}$$

At $t = 3.00$ min, $[\mathrm{A}] = 0.399\,\mathrm{mol\,dm^{-3}}$ and

$$k = \frac{\ln(1.000/0.349)}{3.00\,\mathrm{min}} = 0.351\,\mathrm{min}^{-1} = 5.85 \times 10^{-3}\,\mathrm{s}^{-1}$$

Values of k may be determined in a similar manner at all other times. The average value of k obtained is $\boxed{5.84 \times 10^{-3}\,\mathrm{s}^{-1}}$. The constancy of k, which varies only between 5.83 and $5.85 \times 10^{-3}\,\mathrm{s}^{-1}$ confirms that the reaction is $\boxed{\text{first order}}$. A linear regression of $\ln[\mathrm{A}]$ against t yields the same result. The half-life is (eqn 22.13)

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.84 \times 10^{-3}\,\mathrm{s}^{-1}} = 118.\bar{7}\,\mathrm{s} = \boxed{1.98\,\mathrm{min}}$$

P22.6 Since both reactions are first-order, we have

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

so $[\mathrm{A}] = [\mathrm{A}]_0\mathrm{e}^{-(k_1+k_2)t}$ [22.12b with $k = k_1 + k_2$]

We are interested in the yield of ketene, CH_2CO; call it K:

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

Integrating yields

$$\int_0^{[K]} d[K] = k_2[A]_0 \int_0^t e^{-(k_1+k_2)t} dt$$

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

The percent yield is the amount of K produced compared to complete conversion; since the stoichiometry of reaction (2) is one-to-one, we can write:

$$\% \text{ yield} = \frac{[K]}{[A]_0} \times 100\% = \frac{k_2}{k_1+k_2}(1 - e^{-(k_1+k_2)t}) \times 100\%,$$

which has its maximum value when the reaction reaches completion

$$\text{max } \% \text{ yield} = \frac{k_2}{k_1+k_2} \times 100\% = \frac{4.65 \text{ s}^{-1}}{(3.74 + 4.65) \text{ s}^{-1}} \times 100\% = \boxed{55.4\%}$$

COMMENT. If we are interested in yield of the desired product (ketene) compared to the products of side reactions (products of reaction 1), it makes sense to define the conversion ratio, the ratio of desired product formed to starting material *reacted*, namely

$$\frac{[K]}{[A]_0 - [A]}$$

which works out in this case to be independent of time

$$\frac{[K]}{[A]_0 - [A]} = \frac{k_2}{k_1 + k_2}$$

If a substance reacts by parallel processes of the same order, then the ratio of the amounts of products will be constant and independent of the extent of the reaction, no matter what the order.

Question. Can you demonstrate the truth of the statement made in the above comment?

P22.8 The stoichiometry of the reaction relates product and reaction concentrations as follows:

$$[A] = [A]_0 - 2[B]$$

When the reaction goes to completion, $[B] = [A]_0/2$; hence $[A]_0 = 0.624 \text{ mol dm}^{-3}$. We can therefore tabulate [A], and examine its half-life. 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 (in Figure 22.2), using

$$\ln \frac{[A]_0}{[A]} = k_A t$$

which follows from

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

t/s	0	600	1200	1800	2400
$[B]/(mol\,dm^{-3})$	0	0.089	0.153	0.200	0.230
$[A]/(mol\,dm^{-3})$	0.624	0.446	0.318	0.224	0.164
$\ln \frac{[A]_0}{[A]}$	0	0.34	0.67	1.02	1.34

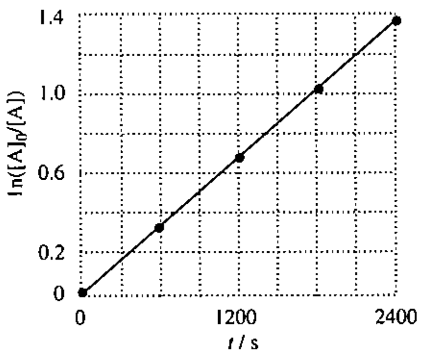


Figure 22.2

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

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

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

P22.10 If the reaction is first-order the concentrations obey

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \text{ [22.12b]}$$

and, since pressures and concentrations of gases are proportional, the pressures should obey

$$\ln\frac{p_0}{p} = kt$$

and $\frac{1}{t}\ln\frac{p_0}{p}$ should be a constant. We test this by drawing up the following table

p_0/Torr	200	200	400	400	600	600
t/s	100	200	100	200	100	200
p_0/Torr	186	173	373	347	559	520
$10^4\left(\frac{1}{t/s}\right)\ln\frac{p_0}{p}$	7.3	7.3	7.0	7.1	7.1	7.2

The values in the last row of the table are virtually constant, and so (in the pressure range spanned by the data) the reaction has $\boxed{\text{first-order kinetics}}$ with $k = \boxed{7.2 \times 10^{-4}\,\mathrm{s}^{-1}}$

P22.12 Using spreadsheet software to evaluate eqn 22.40, one can draw up a plot like that in Figure 22.3. 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 $k_2 = 1\ \mathrm{s}^{-1}$ for all curves and k_1 varies. The thickest curve, labeled 10, corresponds to $k_2 = 10\ \mathrm{s}^{-1}$, 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 $\boxed{\text{steady-state approximation}}$, which becomes more and more valid as consumption of the intermediate becomes fast compared with its formation.

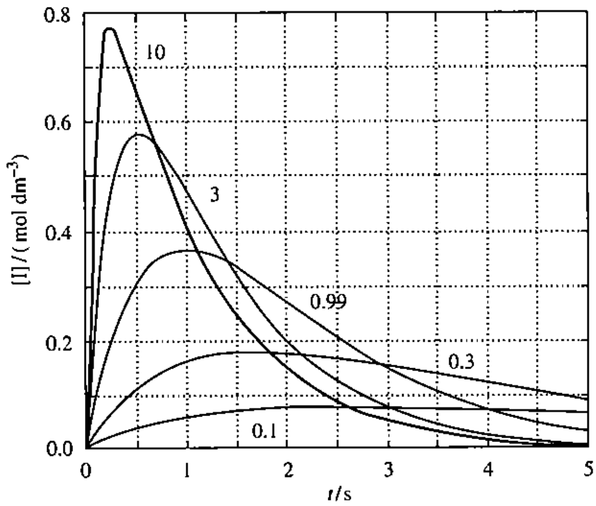


Figure 22.3

P22.14 **(a)** First, find an expression for the relaxation time, using Example 22.4 as a model:

$$\frac{d[A]}{dt} = -2k_a[A]^2 + 2k_b[A_2]$$

Rewrite the expression in terms of a difference from equilibrium values, $[A] = [A]_{eq} + x$:

$$\frac{d[A]}{dt} = \frac{d([A]_{eq} + x)}{dt} = \frac{dx}{dt} = -2k_a([A]_{eq} + x)^2 + 2k_b([A_2]_{eq} - \tfrac{1}{2}x)$$

$$\frac{dx}{dt} = -2k_a[A]^2_{eq} - 4k_a[A]_{eq}x - 2k_ax^2 + 2k_b[A_2]_{eq} - k_bx \approx -(4k_a[A]_{eq} + k_b)x$$

Neglect powers of x greater than x^1, and use the fact that at equilibrium the forward and reverse rates are equal:

$$k_a[A]^2_{eq} = k_b[A_2]_{eq}$$

to obtain

$$\frac{dx}{dt} \approx -(4k_a[A]_{eq} + k_b)x \quad \text{so} \quad \frac{1}{\tau} \approx 4k_a[A]_{eq} + k_b$$

To get the desired expression, square the reciprocal relaxation time,

$$\frac{1}{\tau^2} \approx 16k_a^2[A]_{eq}^2 + 8k_a k_b[A]_{eq} + k_b^2 \qquad (*)$$

introduce $[A]_{tot} = [A]_{eq} + 2[A_2]_{eq}$ into the middle term,

$$\frac{1}{\tau^2} \approx 16k_a^2[A]_{eq}^2 + 8k_a k_b([A]_{tot} - 2[A_2]_{eq}) + k_b^2$$

$$\approx 16k_a^2[A]_{eq}^2 + 8k_a k_b[A]_{tot} - 16k_a k_b[A_2]_{eq} + k_b^2 = \boxed{8k_a k_b[A]_{tot} + k_b^2}$$

and use the equilibrium condition again to see that the remaining equilibrium concentrations cancel each other.

COMMENT. Introducing $[A]_{tot}$ into just one term of eqn * above is a permissible step, but not a very systematic one. It is worth trying because of the resemblance between eqn * and the desired expression: we would be finished if we could get $[A]_{tot}$ into the middle term and somehow get the first term to disappear! A more systematic but messier approach would be to express $[A]_{eq}$ in terms of the desired $[A]_{tot}$ by using the equilibrium condition and $[A]_{tot} = [A]_{eq} + 2[A_2]_{eq}$: solve both of those equations for $[A_2]_{eq}$, set the two resulting expressions equal to each other, solve for $[A]_{eq}$ in terms of the desired $[A]_{tot}$, and substitute **that** expression for $[A]_{eq}$ everywhere in eqn *.

(b) Plot $\frac{1}{\tau^2}$ vs. $[A]_{tot}$. The resulting curve should be a straight line whose y-intercept is k_b^2 and whose slope is $8k_a k_b$.

(c) Draw up the following table:

$[A]_{tot}/(\text{mol dm}^{-3})$	0.500	0.352	0.251	0.151	0.101
τ/ns	2.3	2.7	3.3	4.0	5.3
$1/(\tau/\text{ns})^2$	0.189	0.137	0.092	0.062	0.036

The plot is shown in Figure 22.4.

The y-intercept is 0.0003 ns^{-2} and the slope is 0.38 $\text{ns}^{-2}\ \text{dm}^3\ \text{mol}^{-1}$, so

$$k_b = \{3 \times 10^{-4} \times (10^{-9}\ \text{s})^{-2}\}^{1/2} = (3 \times 10^{14}\ \text{s}^{-2})^{1/2} = \boxed{1.\overline{7} \times 10^7 \text{s}^{-1}}$$

$$\text{and } k_a = \frac{0.38 \times (10^{-9}\ \text{s})^{-2}\text{dm}^3\ \text{mol}^{-1}}{8 \times (1.\overline{7} \times 10^7\ \text{s}^{-1})} = \boxed{2.\overline{7} \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$$

$$K = \frac{k_a/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{k_b/\text{s}^{-1}} = \frac{2.\overline{7} \times 10^9}{1.\overline{7} \times 10^7} = \boxed{1.6 \times 10^2}$$

COMMENT. The data define a good straight line, as the correlation coefficient $R^2 = 0.996$ shows. That straight line appears to go through the origin, but the best-fit equation gives a small non-zero y-intercept. Inspection of the plot shows that several of the data points lie about as far from the fit line as the y-intercept does from zero. This suggests that y-intercept has a fairly high relative uncertainty, and so do the rate constants.

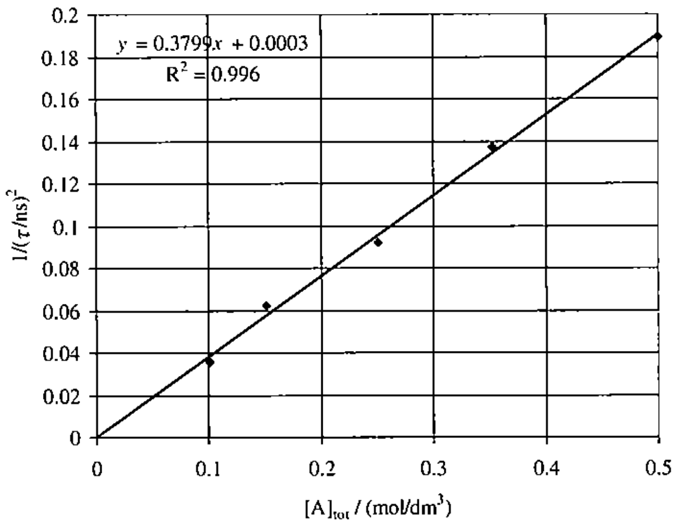


Figure 22.4

P22.16 Apply the equation derived in P22.5 to the rate constant data in pairs

$$E_a = \frac{-R\ln(k/k')}{((1/T)-(1/T'))}$$

T/K	300.3	300.3	341.2
T'/K	341.2	392.2	392.2
$10^{-7}\,k/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	1.44	1.44	3.03
$10^{-7}\,k'/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	3.03	6.9	6.9
$E_a/(\mathrm{kJ\,mol^{-1}})$	15.5	16.7	18.0

The mean is $\boxed{16.7\ \mathrm{kJ\,mol^{-1}}}$. Compute A from each rate constant, using the mean E_a and $A = ke^{E_a/RT}$.

T/K	300.3	341.2	392.2
$10^{-7}\,k/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	1.44	3.03	6.9
E_a/RT	6.69	5.89	5.12
$10^{-10}\,A/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	1.16	1.10	1.16

The mean is $\boxed{1.14\times10^{10}\ \mathrm{dm^3\,mol^{-1}s^{-1}}}$

P22.18 The relation between the equilibrium constant and the rate constants is obtained from

$$\Delta_r G^\ominus = -RT\ln K = \Delta_r H^\ominus - T\Delta_r S^\ominus \quad \text{and} \quad K = \frac{k}{k'}$$

So $K = \dfrac{k}{k'} = \exp\left(\dfrac{-\Delta_r H^\ominus}{RT}\right)\exp\left(\dfrac{\Delta_r S^\ominus}{R}\right) = \left(\dfrac{A}{A'}\right)\exp\left(\dfrac{E_a' - E_a}{RT}\right)$

Setting the temperature-dependent parts equal yields

$$\Delta_r H^\ominus = E_a - E'_a = [-4.2 - (53.3)]\ \text{kJ mol}^{-1} = -57.5\ \text{kJ mol}^{-1}$$

Setting the temperature-independent parts equal yields

$$\exp\left(\frac{\Delta_r S^\ominus}{R}\right) = \left(\frac{A}{A'}\right)$$

so $\Delta_r S^\ominus = R\ln\left(\frac{A}{A'}\right) = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\ln\left(\frac{1.0\times10^9}{1.4\times10^{11}}\right) = -41.1\ \text{J K}^{-1}\ \text{mol}^{-1}$

The thermodynamic quantities of the reaction are related to standard molar quantities

$$\Delta_r H^\ominus = \Delta_f H^\ominus(C_2H_6) + \Delta_f H^\ominus(Br) - \Delta_f H^\ominus(C_2H_5) - \Delta_f H^\ominus(HBr)$$

so $\Delta_f H^\ominus(C_2H_5) = \Delta_f H^\ominus(C_2H_6) + \Delta_f H^\ominus(Br) - \Delta_f H^\ominus(HBr) - \Delta_r H^\ominus$

and $\Delta_f H^\ominus(C_2H_5) = [(-84.68) + 111.88 - (-36.40) - (-57.5)]\ \text{kJ mol}^{-1} = \boxed{121.2\ \text{kJ mol}^{-1}}$

Similarly

$$S_m^\ominus(C_2H_5) = [229.60 + 175.02 - 198.70 - (-41.1)]\ \text{J mol}^{-1}\ \text{K}^{-1} = \boxed{247.0\ \text{J K}^{-1}\ \text{mol}^{-1}}$$

Finally

$$\begin{aligned}\Delta_f G^\ominus(C_2H_5) &= [-32.82 + 82.396 - (-53.45)]\ \text{kJ mol}^{-1} - \Delta_r G^\ominus \\ &= 103.03\ \text{kJ mol}^{-1} - \Delta_r G^\ominus\end{aligned}$$

but

$$\begin{aligned}\Delta_r G^\ominus &= \Delta_r H^\ominus - T\Delta_r S^\ominus = -57.5\ \text{kJ mol}^{-1} - (298\ \text{K})\times(-41.1\times10^{-3}\ \text{kJ K}^{-1}\ \text{mol}^{-1}) \\ &= -45.3\ \text{kJ mol}^{-1}\end{aligned}$$

so $\Delta_f G^\ominus(C_2H_5) = [103.03 - (-45.3)]\ \text{kJ mol}^{-1} = \boxed{148.3\ \text{kJ mol}^{-1}}$

Solutions to theoretical problems

P22.20 We assume a pre-equilibrium (as the initial step is fast), and write

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

The rate-determining step then gives

$$v = \frac{d[P]}{dt} = k_2[A][B] = \boxed{k_2K^{1/2}[A_2]^{1/2}[B]} = k_{\text{eff}}[A_2]^{1/2}[B]$$

where $k_{\text{eff}} = k_2K^{1/2}$.

P22.22 $v = \dfrac{d[\mathrm{P}]}{dt} = k[\mathrm{A}][\mathrm{B}]$

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

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

$$\int_0^t k\,dt = \int_0^x \frac{dx}{(A_0 - 2x) \times (B_0 - 3x)}$$

$$= \int_0^x \left(\frac{6}{2B_0 - 3A_0}\right) \times \left(\frac{1}{3(A_0 - 2x)} - \frac{1}{2(B_0 - 3x)}\right) dx$$

$$= \left(\frac{-1}{2B_0 - 3A_0}\right) \times \left(\int_0^x \frac{dx}{x - (1/2)A_0} - \int_0^x \frac{dx}{x - (1/3)B_0}\right)$$

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

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

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

P22.24 The rate equations are

$$\frac{d[\mathrm{A}]}{dt} = -k_a[\mathrm{A}] + k_a'[\mathrm{B}]$$

$$\frac{d[\mathrm{B}]}{dt} = k_a[\mathrm{A}] - k_a'[\mathrm{B}] - k_b[\mathrm{B}] + k_b'[\mathrm{C}]$$

$$\frac{d[\mathrm{C}]}{dt} = k_b[\mathrm{B}] - k_b'[\mathrm{C}]$$

These equations are a set of coupled differential equations and, though it is not immediately apparent, they do admit of an analytical general solution. However, we are looking for specific circumstances under which the mechanism reduces to the second form given. Since the reaction involves an intermediate, let us explore the result of applying the steady-state approximation to it. Then

$$\frac{d[\mathrm{B}]}{dt} = k_a[\mathrm{A}] - k_a'[\mathrm{B}] - k_b[\mathrm{B}] + k_b'[\mathrm{C}] = 0$$

and $[\mathrm{B}] = \dfrac{k_a[\mathrm{A}] + k_b'[\mathrm{C}]}{k_a' + k_b}$

Therefore, $\dfrac{d[\mathrm{A}]}{dt} = -\dfrac{k_a k_b}{k_a' + k_b}[\mathrm{A}] + \dfrac{k_a' k_b'}{k_a' + k_b}[\mathrm{C}]$

This rate expression may be compared to that given in the text [Section 22.4] for the mechanism

$$\mathrm{A} \underset{k'}{\overset{k}{\rightleftarrows}} \mathrm{B} \quad \left[\text{here } \mathrm{A} \underset{k'_{\text{eff}}}{\overset{k_{\text{eff}}}{\rightleftarrows}} \mathrm{C}\right]$$

Hence, $k_{\text{eff}} = \dfrac{k_a k_b}{k'_a + k_b} \quad k'_{\text{eff}} = \dfrac{k'_a k'_b}{k'_a + k_b}$

The solutions are $[\mathrm{A}] = \left(\dfrac{k'_{\text{eff}} + k_{\text{eff}} e^{-(k'_{\text{eff}}+k_{\text{eff}})t}}{k'_{\text{eff}} + k_{\text{eff}}}\right) \times [\mathrm{A}]_0$ [22.23]

and $[\mathrm{C}] = [\mathrm{A}]_0 - [\mathrm{A}]$

Thus, the conditions under which the first mechanism given reduces to the second are the conditions under which the steady-state approximation holds, namely, when B can be treated as a $\boxed{\text{steady-state intermediate}}$.

P22.26 Let the forward rates be written as

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

and the reverse rates as

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

The net rates are then

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

But $[\mathrm{A}] = [\mathrm{A}]_0$ and $[\mathrm{D}] = 0$, so that the steady-state equations for the net rates of the individual steps are

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

From the second of these equations we find

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

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

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

which yields, upon isolating [B],

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

Thus, at the steady state

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

COMMENT. At steady state, not only are the net rates of reactions 1, 2, and 3 steady, but so are the concentrations [B] and [C]. That is,

$$\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_1[\mathrm{A}]_0 - (k_1' + k_2)[\mathrm{B}] + k_2'[\mathrm{C}] \approx 0$$

and $\dfrac{\mathrm{d[C]}}{\mathrm{d}t} = k_2[\mathrm{B}] - (k_2' + k_3)[\mathrm{C}] \approx 0$

In fact, another approach to solving the problem is to solve these equations for [B] and [C].

P22.28 $$2\,\mathrm{A} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathrm{A}_2 \qquad \frac{\mathrm{d[A]}}{\mathrm{d}t} = -2k_a[\mathrm{A}]^2 + 2k_b[\mathrm{A}_2]$$

Define the deviation from equilibrium x by the following equations, which satisfy the law of mass conservation.

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} + 2x \quad \text{and} \quad [\mathrm{A}_2] = [\mathrm{A}_2]_{\mathrm{eq}} - x$$

Then,

$$\frac{\mathrm{d}([\mathrm{A}]_{\mathrm{eq}} + 2x)}{\mathrm{d}t} = -2k_a([\mathrm{A}]_{\mathrm{eq}} + 2x)^2 + 2k_b([\mathrm{A}_2]_{\mathrm{eq}} - x)$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_a([\mathrm{A}]_{\mathrm{eq}} + 2x)^2 + k_b([\mathrm{A}_2]_{\mathrm{eq}} - x) = -k_a([\mathrm{A}]_{\mathrm{eq}}^2 + 4[\mathrm{A}]_{\mathrm{eq}}x + 4x^2) + k_b([\mathrm{A}_2]_{\mathrm{eq}} - x)$$

$$= -\left\{4k_a x^2 + (k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})x + k_a[\mathrm{A}]_{\mathrm{eq}}^2 - k_b[\mathrm{A}_2]_{\mathrm{eq}}\right\}$$

$$= -\left\{(k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})x + k_a[\mathrm{A}]_{\mathrm{eq}}^2 - k_b[\mathrm{A}_2]_{\mathrm{eq}}\right\}$$

In the last equation the term containing x^2 has been dropped because x will be small near equilibrium and the x^2 term will be negligibly small. The equation may now be rearranged and integrated using the following integration, which is found in standard mathematical handbooks.

$$\int \frac{\mathrm{d}w}{aw + b} = \frac{1}{a}\ln(aw + b)$$

$$\int \frac{\mathrm{d}x}{(k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})x + k_a[\mathrm{A}]_{\mathrm{eq}}^2 - k_b[\mathrm{A}_2]_{\mathrm{eq}}} = -\int \mathrm{d}t + \text{constant}$$

$$\frac{1}{(k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})}\ln((k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})x + k_a[\mathrm{A}]_{\mathrm{eq}}^2 - k_b[\mathrm{A}_2]_{\mathrm{eq}}) = -t + \text{constant}$$

$$\ln\left(\frac{y}{y_0}\right) = -(k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})t \quad \text{where } y = (k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})x + k_a[\mathrm{A}]_{\mathrm{eq}}^2 - k_b[\mathrm{A}_2]_{\mathrm{eq}}$$

$$y = y_0 \mathrm{e}^{-(k_b + 4k_a[\mathrm{A}]_{\mathrm{eq}})t}$$

Comparison of the above exponential to the decay equation $y = y_0 e^{-t/\tau}$ reveals that

$$\tau = \frac{1}{k_b + 4k_a[A]_{eq}}$$

Note that this equation can be used as an alternate derivation of the equation discussed in problem 22.14. The manipulations use the facts that $K = [A_2]_{eq}/[A]_{eq}^2 = k_a/k_b$ and $[A]_{tot} = [A]_{eq} + 2[A_2]_{eq}$ by conservation of mass, which can be used to show that

$$[A]_{tot} = [A]_{eq} + \frac{2k_a}{k_b}[A]_{eq}^2 \quad \text{or} \quad \frac{2k_a}{k_b}[A]_{eq}^2 + [A]_{eq} - [A]_{tot} = 0$$

This quadratic equation can be solved for $[A]_{eq}$.

$$[A]_{eq} = \frac{k_b}{4k_a}\left(\sqrt{1 + \frac{8k_a[A]_{tot}}{k_b}} - 1\right)$$

Substitution of this equation into $\frac{1}{\tau^2} = (k_b + 4k_a[A]_{eq})^2$ and some algebraic manipulation yields the result of problem 22.14: $\frac{1}{\tau^2} = k_b^2 + 8k_a k_b[A]_{tot}$.

Solutions to applications

P22.30 The first-order half-life is related to the rate constant by eqn 22.13

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

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

P22.32 (a) $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

The peak concentration of B, $[P]_n$, immediately after administration of the n^{th} dose, each of which have been administered at the time interval τ, is given by the sum:

$$[P]_n = \underbrace{[B]_0}_{\substack{\text{Conc.}\\ \text{contribution}\\ \text{of } n^{th} \text{ dose}}} + \underbrace{[B]_0 e^{-k_2\tau}}_{\substack{\text{remainder}\\ \text{of } (n-1)^{th}\\ \text{dose}}} + \underbrace{[B]_0 e^{-2k_2\tau}}_{\substack{\text{remainder}\\ \text{of } (n-2)^{th}\\ \text{dose}}} + \cdots\cdots + \underbrace{[B]_0 e^{-(n-1)k_2\tau}}_{\substack{\text{remainder}\\ \text{of } 1^{st}\\ \text{dose}}} = [B]_0 \sum_{m=0}^{n-1} e^{-mk_2\tau}$$

The residual concentration of B, $[R]_n$, just before administration of the $(n+1)^{\text{th}}$ dose results from the first-order elimination of $[P]_n$: $[R]_n = [P]_n e^{-k_2\tau}$ [22.12 a,b],

$$[P]_\infty = \lim_{n\to\infty}[P]_n = [B]_0 \sum_{m=0}^{\infty} e^{-mk_2\tau} = [B]_0\left(1 + x + x^2 + \cdots\right) \text{ where } x = e^{-k_2\tau} < 1$$

This may be simplified using the Taylor series: $1 + x + x^2 + \cdots = \frac{1}{1-x} = \frac{1}{1-e^{-k_2\tau}}$ when $x < 1$

We conclude that $\boxed{[P]_\infty = [B]_0\left(1 - e^{-k_2\tau}\right)^{-1}}$.

Furthermore, $[R]_n = [B]_0 e^{-k_2\tau}\sum\limits_{m=0}^{n-1} e^{-mk_2\tau} = \boxed{[B]_0 \sum\limits_{m=1}^{n} e^{-mk_2\tau}}$.

$$[R]_\infty = [P]_\infty e^{-k_2\tau} = \frac{[B]_0 e^{-k_2\tau}}{1-e^{-k_2\tau}} = \frac{[B]_0}{e^{k_2\tau}-1} = [B]_0\left(e^{k_2\tau}-1\right)^{-1}.$$

$$\begin{aligned}
[P]_\infty - [R]_\infty &= [B]_0\left\{\left(1-e^{-k_2\tau}\right)^{-1} - \left(e^{k_2\tau}-1\right)^{-1}\right\}\\
&= [B]_0\left\{\left(1-e^{-k_2\tau}\right)^{-1} - e^{-k_2\tau}\left(1-e^{-k_2\tau}\right)^{-1}\right\}\\
&= [B]_0\left\{\left(1-e^{-k_2\tau}\right)\left(1-e^{-k_2\tau}\right)^{-1}\right\} = \boxed{[B]_0}.
\end{aligned}$$

(b) (i) Solving the equation $[P]_\infty = [B]_0\left(1-e^{-k_2\tau}\right)^{-1}$ for τ gives:

$$\frac{[B]_0}{[P]_\infty} = 1 - e^{-k_2\tau} \quad \text{or} \quad e^{-k_2\tau} = 1 - \frac{[B]_0}{[P]_\infty} \quad \text{or} \quad -k_2\tau = \ln\left(1 - \frac{[B]_0}{[P]_\infty}\right)$$

$$\tau = -\frac{1}{k_2}\ln\left(1 - \frac{[B]_0}{[P]_\infty}\right) = -\frac{1}{0.0289\ \text{h}^{-1}}\ln\left(1 - \frac{1}{10}\right) = \boxed{3.65\ \text{h}}$$

Figure 22.5(a) shows peak and residual drug concentrations against the number of administrations. Figure 22.5(b) shows the concentration variation with time. It clearly demonstrates the peak and residual concentration and the elimination decay between drug administrations.

(ii) By using the trace function of the plot, or by directly reading the graph, it is found that $[P]_n$ is 75% of the maximum value when $n = \boxed{13}$.

$$\begin{aligned}
t_{75\%\text{max}} &= (n-1)\tau\\
&= (13-1)(3.65\ \text{h})\\
&= 43.8\text{h}
\end{aligned}$$

(iii) The magnitude of the variation $[P]_n - [R]_n$ may be reduced by reducing the drug dosage $[B]_0$. However, in order to avoid changing $[P]_\infty$ it becomes necessary to reduce τ.

(c) For first-order absorption and zero-order elimination of a single dose $[A]_0$:

$$\frac{d[A]}{dt} = k_1[A] \quad \text{and} \quad [A] = [A]_0 e^{-k_1 t} \quad [22.12a, b]$$

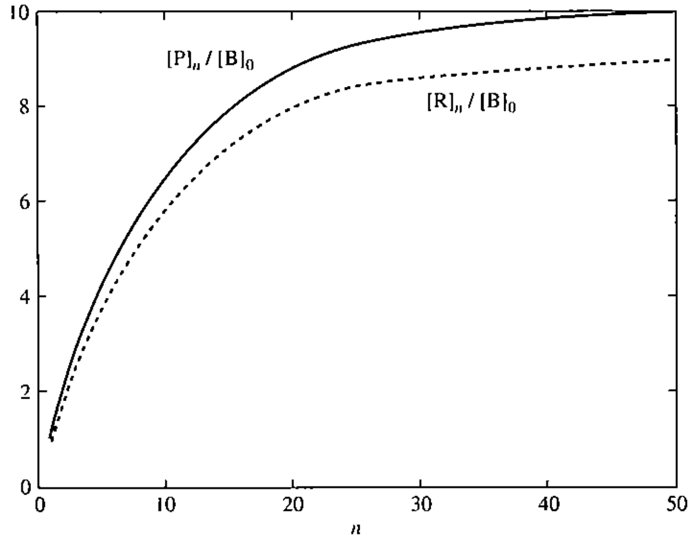


Figure 22.5(a)

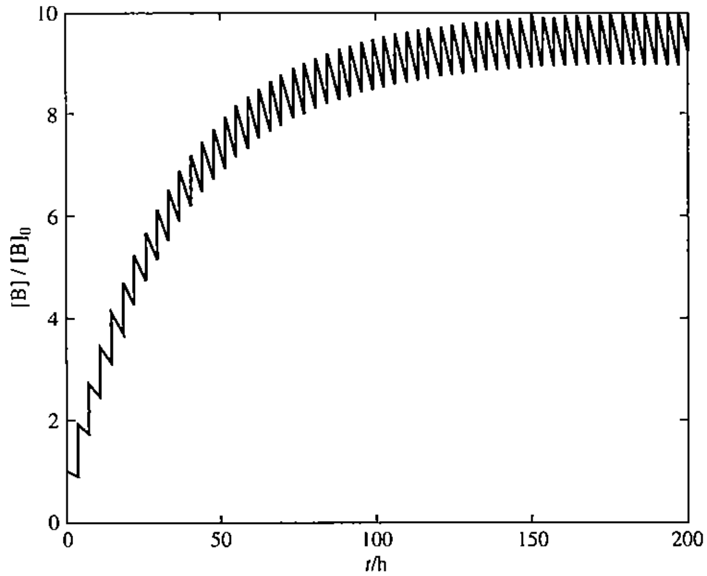


Figure 22.5(b)

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

$$\int_0^{[B]} d[B] = \int_0^t \left(k_1[A]_0 e^{-k_1 t} - k_2\right) dt = k_1[A]_0 \int_0^t e^{-k_1 t} dt - k_2 \int_0^t dt$$

$$\boxed{[B] = [A]_0\left(1 - e^{-k_1 t}\right) - k_2 t}$$

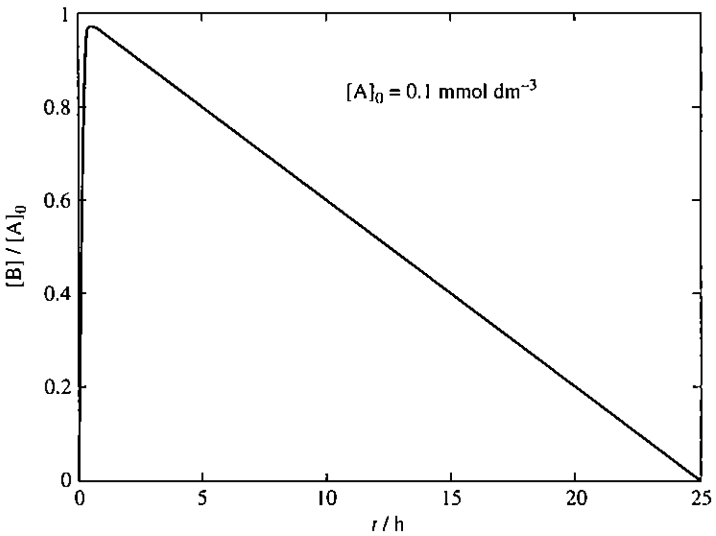


Figure 22.5(c)

The plot of $[B]/[A]_0$ (Figure 22.5(c)) shows rapid absorption of the drug into the blood followed by the slower, linear elimination that corresponds to zeroth-order elimination. Elimination occurs within 25 h with these rate constants.

(d) Let $\{[B]_{max}, t_{max}\}$ be the maximum of a curve such as that shown above. To find formulas for this point, we must examine the curve at the point for which $d[B]/dt = 0$.

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t_{max}} - k_2 = 0$$

$$e^{-k_1 t_{max}} = \frac{k_2}{k_1[A]_0} \quad \text{or} \quad -k_1 t_{max} = \ln\left(\frac{k_2}{k_1[A]_0}\right)$$

$$\boxed{t_{max} = \frac{1}{k_1}\ln\left(\frac{k_1[A]_0}{k_2}\right)}.$$

$$[B]_{max} = [A]_0\left(1 - e^{-k_1 t_{max}}\right) - k_2 t_{max} = [A]_0\left(1 - e^{-k_1 \frac{1}{k_1}\ln\left(\frac{k_1[A]_0}{k_2}\right)}\right) - k_2 t_{max}$$

$$= [A]_0\left(1 - e^{\ln\left(\frac{k_2}{k_1[A]_0}\right)}\right) - k_2 t_{max} = [A]_0\left(1 - \frac{k_2}{k_1[A]_0}\right) - k_2 t_{max}$$

$$\boxed{[B]_{max} = [A]_0 - \frac{k_2}{k_1} - k_2 t_{max}}.$$

P22.34 Analysis of NMR lineshapes can be used to infer time scales of protein folding or unfolding steps. Protons (or other nuclei, for that matter) that have different chemical shifts in folded and unfolded proteins will yield a single peak if the time scale for interconversion (i.e. for folding or unfolding) is comparable to or less than the reciprocal of the two peaks' frequency difference. Monitoring the change from two peaks (indicating that a sample contains both folded and unfolded proteins, which might be observed at one temperature) to a broad single peak (indicating fast interconversion, which might be the case at a higher temperature) can allow the determination of the time constant for the conversion. One advantage of

NMR over vibrational or electronic spectroscopy is that the radiation used to probe the system is much less energetic, and therefore much less likely to alter the folding or unfolding process it is designed to investigate. The lineshape strategy cannot be used to investigate processes as fast as those accessible by electronic or vibrational spectroscopy. (cf. Example 15.2.)

P22.36 First, turn eqn 22.30 into an expression involving the functional forms given in the data:

$$E_a = RT^2\frac{d\ln k}{dT} = RT^2\frac{d\ln k}{d(1/T)}\frac{d(1/T)}{dT} = -R\frac{d\ln k}{d(1/T)} = -R\ln(10)\frac{d\log k}{d(1/T)}$$

$$= -R\ln(10)\frac{d}{d(1/T)}\left(11.75 - \frac{5488}{T/K}\right) = -(8.3145\,J\,K^{-1}\,mol^{-1})\ln(10)(-5488\,K)$$

$$= \boxed{105\,kJ\,mol^{-1}}$$

$$\Delta_r G^{\oplus} = -RT\ln K = -RT\ln(10)\log K \text{ [section 7.2d for } \Delta_r G^{\oplus}]$$

At 298.15 K

$$\Delta_r G^{\oplus} = -(8.3145\,J\,K^{-1}\,mol^{-1}) \times (298.15\,K)\ln(10)\left(-1.36 + \frac{1794}{298.15}\right)$$

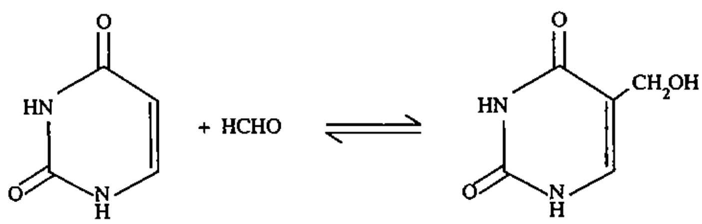
$$\Delta_r G^{\oplus} = \boxed{-26.6\,kJ\,mol^{-1}}$$

$$\Delta_r H^{\oplus} = -R\frac{d\ln(K)}{d(1/T)}\text{ [7.23b]} = -R\ln(10)\frac{d\log(K)}{d(1/T)}$$

$$= -R\ln(10)\frac{d}{d(1/T)}\left(-1.36 + \frac{1794}{T/K}\right) = -(8.3145\,J\,K^{-1}\,mol^{-1})\ln(10)(1794\,K)$$

$$= \boxed{-34.3\,kJ\,mol^{-1}}$$

The reaction is



The equations for the rate constant k and the equilibrium constant K were obtained under conditions corresponding to the biological standard state (pH = 7, p = 1 bar; Section 7.2d). Thus the values of $\Delta_r G$ calculated from the equation for K are $\Delta_r G^{\oplus}$ values which can differ significantly from $\Delta_r G^{\ominus}$ (pH = 1, p = 1 bar). Prebiotic conditions are more likely to be near pH = 7 than pH = 1 so we expect that the reaction will still be favorable ($K \gg 1$) thermodynamically.

Because $\Delta_r G = \Delta_r G^{\oplus} + RT\ln Q$ [7.11] and since we might expect $Q < 1$ in a prebiotic environment, $\Delta_r G < \Delta_r G^{\oplus}$. But, as shown in the calculation above, $\Delta_r G^{\oplus}$ is rather large and negative (−26.6 kJ mol^{-1}), so we expect it will still be large and negative under the prebiotic conditions; hence the reaction will be spontaneous for these conditions. We expect that $\Delta_r H \approx \Delta_r H^{\oplus}$ because enthalpy changes largely reflect bond breakage and bond formation energies.

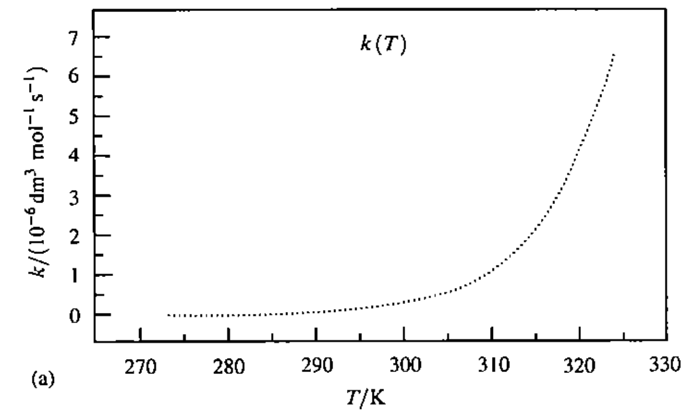


Figure 22.6(a)

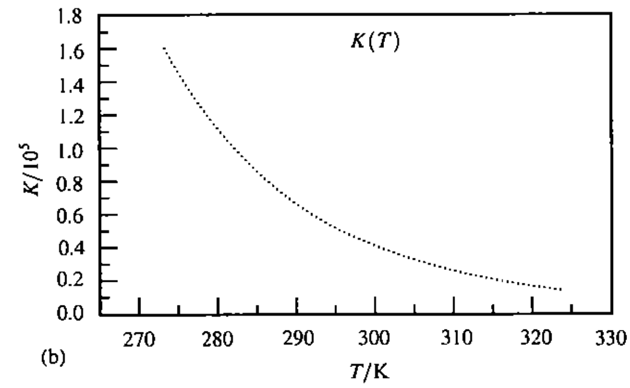


Figure 22.6(b)

A plot of the equation for the rate constant k is shown in Figure 22.6(a) and that for the equilibrium constant in Figure 22.6(b). From a kinetic point of view the reaction becomes more favorable at higher temperatures; from a thermodynamic point of view it becomes less favorable, but $K \gg 1$ at all temperatures.

P22.38 (a) The rate of reaction is

$$v = k[CH_4][OH]$$

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

$$\times (4.0 \times 10^{-8}\,\mathrm{mol\,dm^{-3}}) \times (1.5 \times 10^{-15}\,\mathrm{mol\,dm^{-3}}) = \boxed{1.1 \times 10^{-16}\,\mathrm{mol\,dm^{-3}s^{-1}}}$$

(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.

$$m = MvVt = (0.01604\ \text{kg mol}^{-1}) \times (1.1 \times 10^{-16}\ \text{mol dm}^{-3}\ \text{s}^{-1})$$

$$\times (4 \times 10^{21}\ \text{dm}^3) \times (365 \times 24 \times 3600\ \text{s})$$

$$= \boxed{2.2 \times 10^{11}\ \text{kg or } 220\ \text{Tg}}$$

P22.40 The initial rate is

$$v_0 = (3.6 \times 10^6\ \text{dm}^9\ \text{mol}^{-3}\ \text{s}^{-1}) \times (5 \times 10^{-4}\ \text{mol dm}^{-3})^2 \times (10^{-4.5}\ \text{mol dm}^{-3})^2$$

$$= \boxed{9 \times 10^{-10}\ \text{mol dm}^{-3}\ \text{s}^{-1}}$$

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

$$-\frac{\text{d}[\text{HSO}_3^-]}{\text{d}t} = k'[\text{HSO}_3^-]^2$$

Comparison to the given rate law and rate constant shows

$$k' = 2k[\text{H}^+]^2 = 2(3.6 \times 10^6\ \text{dm}^9\text{mol}^{-3}\ \text{s}^{-1}) \times (10^{-4.5}\ \text{mol dm}^{-3})^2$$

$$= 7.2 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

and $t_{1/2} = \dfrac{1}{(7.2 \times 10^{-3}\ \text{dm}^3\ \text{mol}^{-1}\text{s}^{-1}) \times (5 \times 10^{-4}\ \text{mol dm}^{-3})} = \boxed{2.\bar{8} \times 10^5\ \text{s} = 3\ \text{days}}$

23 The kinetics of complex reactions

Answers to discussion questions

D23.2 In the analysis of stepwise polymerization, the rate constant for the second-order condensation is assumed to be independent of the chain length and to remain constant throughout the reaction. It follows, then, that the degree of polymerization is given by

$$\langle n \rangle = 1 + kt[\mathrm{A}]_0$$

Therefore, the average molar mass can be controlled by adjusting the initial concentration of monomer and the length of time that the polymerization is allowed to proceed.

Chain polymerization is a complicated radical chain mechanism involving initiation, propagation, and termination steps (see Section 23.4 for the details of this mechanism). The derivation of the overall rate equation utilizes the steady state approximation and leads to the following expression for the average number of monomer units in the polymer chain:

$$\langle n \rangle = 2k\,[\mathrm{M}]\,[\mathrm{I}]^{-1/2},$$

where $k = (1/2)k_\mathrm{P}\,(fk_\mathrm{i}k_\mathrm{t})^{-1/2}$, with k_P, k_i, and k_t, being the rate constants for the propagation, initiation, and termination steps, and f is the fraction of radicals that successfully initiate a chain. We see that the average molar mass of the polymer is directly proportional to the monomer concentration, and inversely proportional to the square root of the initiator concentration and to the rate constant for initiation. Therefore, the slower the initiation of the chain, the higher the average molar mass of the polymer.

D23.4 Refer to eqns 23.26 and 23.27, which are the analogues of the Michaelis–Menten and Lineweaver–Burk equations (23.21 and 23.22), as well as to Figure 23.13. There are three major modes of inhibition that give rise to distinctly different kinetic behavior (Figure 23.13). In competitive inhibition the inhibitor binds only to the active site of the enzyme and thereby inhibits the attachment of the substrate. This condition corresponds to $\alpha > 1$ and $\alpha' = 1$ (because ESI does not form). The slope of the Lineweaver–Burk plot increases by a factor of α relative to the slope for data on the uninhibited enzyme ($\alpha = \alpha' = 1$). The y-intercept does not change as a result of competitive inhibition. In uncompetitive inhibition, the inhibitor binds to a site of the enzyme that is removed from the active site, but only if the substrate is already present. The inhibition occurs because ESI reduces the concentration of ES, the active type of the complex. In this case $\alpha = 1$ (because EI does not form) and $\alpha' > 1$. The y-intercept of the Lineweaver–Burk plot increases by a factor of α' relative to the y-intercept for data on the uninhibited enzyme, but the slope does not change. In non-competitive inhibition, the inhibitor binds to a site other than the active site, and its presence reduces the ability of the substrate to bind to the active site. Inhibition occurs at both the E and ES sites. This condition corresponds to $\alpha > 1$ and $\alpha' > 1$. Both the slope and y-intercept of the Lineweaver–Burk plot increase upon addition of the inhibitor. Figure 23.13c shows the special case of $K_I = K_I'$ and $\alpha = \alpha'$, which results in intersection of the lines at the x-axis.

In all cases, the efficiency of the inhibitor may be obtained by determining K_M and v_{max} from a control experiment with uninhibited enzyme and then repeating the experiment with a known concentration of inhibitor. From the slope and y-intercept of the Lineweaver–Burk plot for the inhibited enzyme (eqn 23.27), the mode of inhibition, the values of α or α', and the values of K_I, or K_I' may be obtained.

D23.6 The shortening of the lifetime of an excited state is called quenching. Quenching effects may be studied by monitoring the emission from the excited state that is involved in the photochemical process. The addition of a quencher opens up an additional channel for the deactivation of the excited singlet state.

Three common mechanisms for bimolecular quenching of an excited singlet (or triplet) state are:

Collisional deactivation:	$S^* + Q \rightarrow S + Q$
Energy transfer:	$S^* + Q \rightarrow S + Q^*$
Electron transfer:	$S^* + Q \rightarrow S^+ + Q^-$ or $S^- + Q^+$

Collisional quenching is particularly efficient when Q is a heavy species, such as iodide ion, which receives energy from S* and then decays primarily by internal conversion to the ground state. Pure collisional quenching can be detected by the appearance of vibrational and rotational excitation in the spectrum of the acceptor.

In many cases, it is possible to prove that energy transfer is the predominant mechanism of quenching if the excited state of the acceptor fluoresces or phosphoresces at a characteristic wavelength. In a pulsed laser experiment, the rise in fluorescence intensity from Q* with a characteristic time which is the same as that for the decay of the fluorescence of S* is often taken as indication of energy transfer from S to Q.

Electron transfer can be studied by time-resolved spectroscopy (Section 14.6e). The oxidized and reduced products often have electronic absorption spectra distinct from those of their neutral parent compounds. Therefore, the rapid appearance of such known features in the absorption spectrum after excitation by a laser pulse may be taken as indication of quenching by electron transfer.

Solutions to exercises

In the following exercises and problems, it is recommended that rate constants are labeled with the number of the step in the proposed reaction mechanism and that any reverse steps are labeled similarly but with a prime.

E23.1(b) The intermediates are NO and NO_3 and we apply the steady-state approximation to each of their concentrations

$$k_2\,[NO_2]\,[NO_3] - k_3\,[NO]\,[N_2O_5] = 0$$

$$k_1\,[N_2O_5] - k_1'\,[NO_2]\,[NO_3] - k_2\,[NO_2]\,[NO_3] = 0$$

$$\text{Rate} = -\frac{1}{2}\frac{d\,[N_2O_5]}{dt}$$

$$\frac{d\,[N_2O_5]}{dt} = -k_1\,[N_2O_5] + k_1'[NO_2][NO_3] - k_3[NO][N_2O_5]$$

From the steady-state equations

$$k_3[\mathrm{NO}][\mathrm{N_2O_5}] = k_2[\mathrm{NO_2}][\mathrm{NO_3}]$$

$$[\mathrm{NO_2}][\mathrm{NO_3}] = \frac{k_1[\mathrm{N_2O_5}]}{k_1' + k_2}$$

Substituting,

$$\frac{\mathrm{d}[\mathrm{N_2O_5}]}{\mathrm{d}t} = -k_1[\mathrm{N_2O_5}] + \frac{k_1'k_1}{k_1'+k_2}[\mathrm{N_2O_5}] - \frac{k_2k_1}{k_1'+k_2}[\mathrm{N_2O_5}] = -\frac{2k_1k_2}{k_1'+k_2}[\mathrm{N_2O_5}]$$

$$\text{Rate} = \frac{k_1k_2}{k_1'+k_2}[\mathrm{N_2O_5}] = k[\mathrm{N_2O_5}]$$

E23.2(b)

$$\frac{\mathrm{d}[\mathrm{R}]}{\mathrm{d}t} = 2k_1[\mathrm{R_2}] - k_2[\mathrm{R}][\mathrm{R_2}] + k_3[\mathrm{R'}] - 2k_4[\mathrm{R}]^2$$

$$\frac{\mathrm{d}[\mathrm{R'}]}{\mathrm{d}t} = k_2[\mathrm{R}][\mathrm{R_2}] - k_3[\mathrm{R'}]$$

Apply the steady-state approximation to both equations

$$2k_1[\mathrm{R_2}] - k_2[\mathrm{R}][\mathrm{R_2}] + k_3[\mathrm{R'}] - 2k_4[\mathrm{R}]^2 = 0$$

$$k_2[\mathrm{R}][\mathrm{R_2}] - k_3[\mathrm{R'}] = 0$$

The second solves to $[\mathrm{R'}] = \dfrac{k_2}{k_3}[\mathrm{R}][\mathrm{R_2}]$

and then the first solves to $[\mathrm{R}] = \left(\dfrac{k_1}{k_4}[\mathrm{R_2}]\right)^{1/2}$

Therefore, $\dfrac{\mathrm{d}[\mathrm{R_2}]}{\mathrm{d}t} = -k_1[\mathrm{R_2}] - k_2[\mathrm{R_2}][\mathrm{R}] = \boxed{k_1[\mathrm{R_2}] - k_2\left(\dfrac{k_1}{k_4}\right)^{1/2}[\mathrm{R_2}]^{3/2}}$

E23.3(b) **(a)** The figure suggests that a chain-branching explosion $\boxed{\text{does not occur}}$ at temperatures as low as 700 K. There may, however, be a thermal explosion regime at pressures in excess of 10^6 Pa.

(b) The lower limit seems to occur when

$$\log(p/\mathrm{Pa}) = 2.1 \quad \text{so} \quad p = 10^{2.1}\,\mathrm{Pa} = \boxed{1.3\times10^2\,\mathrm{Pa}}$$

There does not seem to be a pressure above which a steady reaction occurs. Rather the chain-branching explosion range seems to run into the thermal explosion range around

$$\log(p/\mathrm{Pa}) = 4.5 \quad \text{so} \quad p = 10^{4.5}\,\mathrm{Pa} = \boxed{3\times10^4\,\mathrm{pa}}$$

E23.4(b) The rate of production of the product is

$$\frac{\mathrm{d}[\mathrm{BH^+}]}{\mathrm{d}t} = k_2[\mathrm{HAH^+}][\mathrm{B}]$$

HAH^+ is an intermediate involved in a rapid pre-equilibrium

$$\frac{[HAH^+]}{[HA][H^+]} = \frac{k_1}{k_1'} \text{ so } [HAH^+] = \frac{k_1 [HA][H^+]}{k_1'}$$

and $$\frac{d[BH^+]}{dt} = \boxed{\frac{k_1 k_2}{k_1'} [HA][H^+][B]}$$

This rate law can be made independent of $[H^+]$ if the source of H^+ is the acid HA, for then H^+ is given by another equilibrium

$$\frac{[H^+][A^-]}{[HA]} = K_a = \frac{[H^+]^2}{[HA]} \text{ so } [H^+] = (K_a[HA])^{1/2}$$

and $$\frac{d[BH^+]}{dt} = \boxed{\frac{k_1 k_2 K_a^{1/2}}{k_1'} [HA]^{3/2}[B]}$$

E23.5(b) A_2 appears in the initiation step only.

$$\frac{d[A_2]}{dt} = -k_1 [A_2]$$

Consequently, the rate of consumption of $[A_2]$ is first order in A_2 and the rate is independent of intermediate concentrations.

E23.6(b) The maximum velocity is $k_b [E]_0$ and the velocity in general is

$$v = k[E]_0 = \frac{k_b [S][E]_0}{K_M + [S]} \text{ so } v_{max} = k_b [E]_0 = \frac{K_M + [S]}{[S]} v$$

$$v_{max} = \frac{(0.042 + 0.890)\ \text{mol dm}^{-3}}{0.890\ \text{mol dm}^{-3}} (2.45 \times 10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}) = \boxed{2.57 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}$$

E23.7(b) The quantum yield tells us that each mole of photons absorbed causes 1.2×10^2 moles of A to react; the stoichiometry tells us that 1 mole of B is formed for every mole of A which reacts. From the yield of 1.77 mmol B, we infer that 1.77 mmol A reacted, caused by the absorption of 1.77×10^{-3} mol/(1.2×10^2 mol Einstein^{-1}) = $\boxed{1.5 \times 10^{-5} \text{ moles of photons}}$

E23.8(b) The quantum efficiency is defined as the amount of reacting molecules n_A divided by the amount of photons absorbed n_{abs}. The fraction of photons absorbed f_{abs} is one minus the fraction transmitted f_{trans}; and the amount of photons emitted n_{photon} can be inferred from the energy of the light source (power P times time t) and the energy of the photons (hc/λ).

$$\Phi = \frac{n_A hc N_A}{(1 - f_{trans})\lambda P t}$$

$$= \frac{(0.324\ \text{mol}) \times (6.626 \times 10^{-34}\ \text{J s}) \times (2.998 \times 10^8\ \text{m s}^{-1}) \times (6.022 \times 10^{23}\ \text{mol}^{-1})}{(1 - 0.257) \times (320 \times 10^{-9}\ \text{m}) \times (87.5\ \text{W}) \times (28.0\ \text{min}) \times (60\ \text{s min}^{-1})}$$

$$= \boxed{1.11}$$

Solutions to problems

Solutions to numerical problems

P23.2 $O + Cl_2 \rightarrow ClO + Cl \quad p(Cl_2) \approx$ constant $\left[Cl_2 \text{ at high pressure}\right]$

Therefore, the reaction is probably pseudo-first order, and

$$[O] \approx [O]_0 \, e^{-k't}$$

That being so, $\ln \dfrac{[O]_0}{[O]} = k't = k[Cl_2]t = k[Cl_2] \times \dfrac{d}{v}$

where $k' = [Cl_2]k$, v is the flow rate, and d is the distance along the tube. We draw up the following table

d/cm	0	2	4	6	8	10	12	14	16	18
$\ln \dfrac{[O]_0}{[O]}$	0.27	0.31	0.34	0.38	0.45	0.46	0.50	0.55	0.56	0.60

The points are plotted in Figure 23.1.

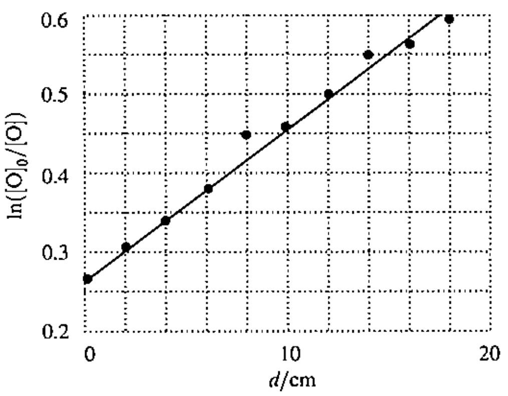


Figure 23.1

The slope is 0.0189, and so $\dfrac{k[Cl_2]}{v} = 0.0189\,\text{cm}^{-1}$.

$$\text{Therefore, } k = \frac{(0.0189\,\text{cm}^{-1}) \times v}{[Cl_2]}$$

$$= \frac{(0.0189\,\text{cm}^{-1}) \times (6.66 \times 10^2\,\text{cm s}^{-1})}{2.54 \times 10^{-7}\,\text{mol dm}^{-3}} = \boxed{5.0 \times 10^7\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

(There is a very fast $O + ClO \rightarrow Cl + O_2$ reaction, and so the answer given here is actually twice the true value.)

P23.4

$H_2 \rightarrow 2H\cdot$	initiation,	$v = v_{init}$
$H\cdot + O_2 \rightarrow \cdot OH + \cdot O\cdot$	branching,	$v = k_1 [H\cdot][O_2]$
$\cdot O\cdot + H_2 \rightarrow \cdot OH + H\cdot$	branching,	$v = k_2 [\cdot O\cdot][H_2]$
$H\cdot + O_2 \rightarrow HO_2\cdot$	propagation,	$v = k_3 [H\cdot][O_2]$
$HO_2\cdot + H_2 \rightarrow H_2O + \cdot OH$	propagation,	$v = k_4 [HO_2\cdot][H_2]$
$HO_2\cdot + \text{wall} \rightarrow \text{destruction}$	termination,	$v = k_5 [HO_2\cdot]$
$H\cdot + M \rightarrow \text{destruction}$	termination,	$v = k_6 [H\cdot][M]$

We identify the onset of explosion with the rapid increase in the concentration of radicals which we initially identify with $[H\cdot]$. Then

$$v_{rad} = v_{init} - k_1 [H\cdot][O_2] + k_2 [\cdot O\cdot][H_2] - k_3 [H\cdot][O_2] - k_6 [H\cdot][M]$$

Intermediates are examined with the steady-state approximation.

$$\frac{d[\cdot O\cdot]}{dt} = k_1 [H\cdot][O_2] - k_2 [\cdot O\cdot][H_2] \approx 0$$

$$[\cdot O\cdot]_{SS} \approx \frac{k_1 [H\cdot][O_2]}{k_2 [H_2]}$$

Therefore,

$$\begin{aligned} v_{rad} &= v_{init} - k_1 [H\cdot][O_2] + k_2 \left(\frac{k_1 [H\cdot][O_2]}{k_2 [H_2]}\right)[H_2] - k_3 [H\cdot][O_2] - k_6 [H\cdot][M] \\ &= v_{init} - (k_3 [O_2] + k_6 [M])[H\cdot] \end{aligned}$$

The factor $(k_3 [O_2] + k_6 [M])$ is always positive and, therefore, v_{rad} always decreases for all values of $[H\cdot]$. No explosion is possible according to this mechanism, or at least no exponential growth of $[H\cdot]$ is observed.

Let us try a second approach for which the concentration of radicals is identified with $[\cdot O\cdot]$.

$$v_{rad} = k_1 [H\cdot][O_2] - k_2 [\cdot O\cdot][H_2]$$

Using the steady-state approximation to describe $[H\cdot]$, we find that

$$[H\cdot]_{SS} = \frac{v_{init} + k_2 [H_2][\cdot O\cdot]}{(k_1 + k_3)[O_2] + k_6 [M]}$$

$$v_{rad} = \frac{v_{init} k_1 [O_2]}{(k_1 + k_3)[O_2] + k_6 [M]} + \left\{\frac{k_1 k_2 [H_2][O_2]}{(k_1 + k_3)[O_2] + k_6 [M]} - k_2 [H_2]\right\}[\cdot O\cdot]$$

This has the form

$$v_{rad} = \frac{d[\cdot O\cdot]}{dt} = C_1 + \{C_2 - C_3\}[\cdot O\cdot]$$

where C_1, C_2, and C_3 are always positive. This means that the mechanism predicts exponential growth of radicals, and explosion, when $C_2 > C_3$. This will occur when $k_1 [O_2]/((k_1 + k_3)[O_2] + k_6 [M]) > 1$. But this is not possible. So no exponential growth of $[\cdot O\cdot]$ can occur. The proposed mechanism is inconsistent with the existence of an explosion on the assumption that the steady-state approximation can be applied to the intermediates H and ·O·. It is, however, unlikely that the steady-state approximation can be applied to explosive reactions, and this is where the analysis breaks down.

P23.6

$$UO_2^{2+} + h\nu \rightarrow (UO_2^{2+})^*$$
$$(UO_2^{2+})^* + (COOH)_2 \rightarrow UO_2^{2+} + H_2O + CO_2 + CO$$
$$2MnO_4^- + 5(COOH)_2 + 6H^+ \rightarrow 10CO_2 + 8H_2O + 2Mn^{2+}$$

$17.0\,cm^3$ of $0.212\,M\,KMnO_4$ is equivalent to

$$\tfrac{5}{2} \times (17.0\,cm^3) \times (0.212\,mol\,dm^{-3}) = 9.01 \times 10^{-3}\,mol\,(COOH)_2$$

The initial sample contained $5.232\,g\,(COOH)_2$, corresponding to

$$\frac{5.232\,g}{90.04\,g\,mol^{-1}} = 5.81 \times 10^{-2}\,mol\,(COOH)_2$$

Therefore, $(5.81 \times 10^{-2}\,mol) - (9.01 \times 10^{-3}\,mol) = 4.91 \times 10^{-2}\,mol$ of the acid has been consumed. A quantum efficiency 0.53 implies that the amount of photons absorbed must have been

$$\frac{4.91 \times 10^{-2}\,mol}{0.53} = 9.3 \times 10^{-2}\,mol$$

Since the exposure was for 300 s, the rate of incidence of photons was

$$\frac{9.3 \times 10^{-2}\,mol}{300\,s} = 3.1 \times 10^{-4}\,mol\,s^{-1}$$

Since 1 mol photons = 1 einstein, the incident rate is $\boxed{3.1 \times 10^{-4}\,einstein\,s^{-1}}$ or $\boxed{1.9 \times 10^{20}\,s^{-1}}$

P23.8

$$M + h\nu_i \rightarrow M^*, \quad I_a\,[M = \text{benzophenone}]$$
$$M^* + Q \rightarrow M + Q, \quad k_q$$
$$M^* \rightarrow M + h\nu_f, \quad k_f$$

$$\frac{d[M^*]}{dt} = I_a - k_f[M^*] - k_q[Q][M^*] \approx 0\ [\text{steady state}]$$

and hence $[M^*] = \dfrac{I_a}{k_f + k_q[Q]}$

Then $I_f = k_f[M^*] = \dfrac{k_f I_a}{k_f + k_q[Q]}$

and so $\boxed{\dfrac{1}{I_f} = \dfrac{1}{I_a} + \dfrac{k_q[Q]}{k_f I_a}}$

If the exciting light is extinguished, $[M^*]$, and hence I_f, decays as $e^{-k_f t}$ in the absence of a quencher. Therefore we can measure $k_q/k_f I_a$ from the slope of $1/I_f$ plotted against [Q], and then use k_f to determine k_q.

We draw up the following table

$10^3\,[\mathrm{Q}]/\mathrm{M}$	1	5	10
$1/I_f$	2.4	4.0	6.3

The points are plotted in Figure 23.2.

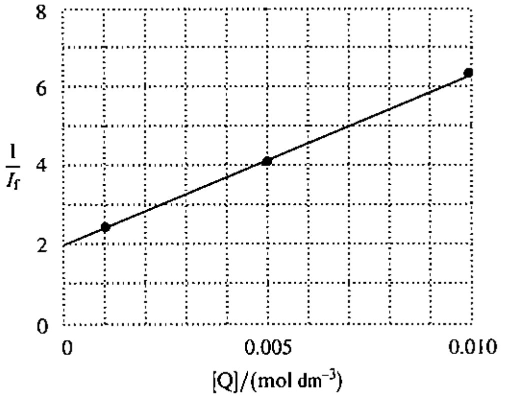


Figure 23.2

The intercept lies at 2.0, and so $I_a = 1/2.0 = 0.50$. The slope is 430, and so

$$\frac{k_q}{k_f I_a} = 430\,\mathrm{dm^3\,mol^{-1}}$$

Then, since $I_a = 0.50$ and $k_f = \dfrac{\ln 2}{t_{1/2}}$,

$$k_q = (0.50) \times \left(430\,\mathrm{dm^3\,mol^{-1}}\right) \times \left(\frac{\ln 2}{29 \times 10^{-6}\,\mathrm{s}}\right) = \boxed{5.1 \times 10^6\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

P23.10 $$E_T = \frac{R_0^6}{R_0^6 + R^6} \quad \text{or} \quad \frac{1}{E_T} = 1 + (R/R_0)^6 \quad [23.38]$$

Since a plot of E_T^{-1} values against R^6 (Figure 23.3) appears to be linear with an intercept equal to 1, we conclude that eqn 23.38 adequately describes the data. Solving eqn 23.38 for R_0 gives $R_0 = R(E_T^{-1} - 1)^{1/6}$. R_0 may be evaluated by taking the mean of experimental data in this expression. The two data points at lowest R must be excluded from the mean as they are highly uncertain. $\boxed{R_0 = 3.5\bar{2}\,\mathrm{nm}}$ with a standard deviation of $0.17\bar{3}$ nm.

Solutions to theoretical problems

P23.12

$$\mathrm{CH_3CHO \rightarrow \cdot CH_3 + \cdot CHO}, \qquad k_a$$

$$\mathrm{\cdot CH_3 + CH_3 \cdot CHO \rightarrow \cdot CH_4 + CH_2 \cdot CHO}, \qquad k_b$$

$$\mathrm{\cdot CH_2CHO \rightarrow CO + \cdot CH_3}, \qquad k_c$$

$$\mathrm{\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3}, \qquad k_d$$

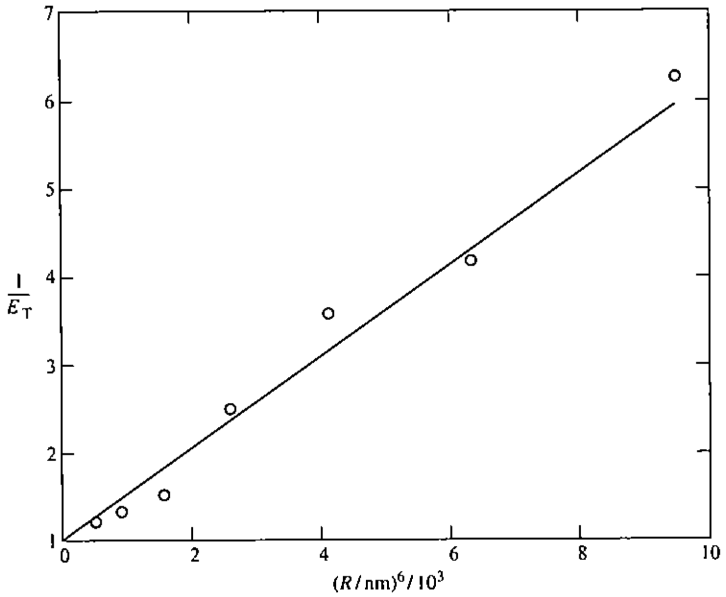


Figure 23.3

$$\frac{d[CH_4]}{dt} = -k_b [CH_3][CH_3CHO]$$

$$\frac{d[CH_3CHO]}{dt} = -k_a [CH_3CHO] - k_b [CH_3CHO][CH_3]$$

$$\frac{d[CH_3]}{dt} = k_a [CH_3CHO] - k_b [CH_3CHO][CH_3] + k_c [CH_2CHO] - 2k_d [CH_3]^2 = 0$$

$$\frac{d[CH_2CHO]}{dt} = k_b [CH_3][CH_3CHO] - k_c [CH_2CHO] = 0$$

Adding the last two equations gives

$$k_a[CH_3CHO] - 2k_d[CH_3]^2 = 0, \quad \text{or} \quad [CH_3] = \left(\frac{k_a}{2k_d}\right)^{1/2} [CH_3CHO]^{1/2}$$

Therefore

$$\frac{d[CH_4]}{dt} = k_b \left(\frac{k_a}{2k_d}\right)^{1/2} [CH_3CHO]^{3/2}$$

$$\frac{d[CH_3CHO]}{dt} = -k_a[CH_3CHO] - k_b \left(\frac{k_a}{2k_d}\right)^{1/2} [CH_3CHO]^{3/2}$$

Note that, to lowest order in k_a,

$$\frac{d[CH_3CHO]}{dt} \approx -k_b \left(\frac{k_a}{2k_d}\right)^{1/2} [CH_3CHO]^{3/2}$$

and the reaction is three-halves order in CH_3CHO.

P23.14 (a) $\overline{M}_{\rm n}^3 = M^3 \sum_n n^3 P_n = M^3(1-p)\sum_n n^3 p^{n-1}$ $[P_n = p^{n-1}(1-p)$, Problem 23.13]

$$= M^3(1-p)\frac{d}{dp}\sum_n n^2 p^n = M^3(1-p)\frac{d}{dp}p\frac{d}{dp}p\frac{d}{dp}\sum_n p^n$$

$$= M^3(1-p)\frac{d}{dp}p\frac{d}{dp}p\frac{d}{dp}(1-p)^{-1} = \frac{M^3(1+4p+p^2)}{(1-p)^3}$$

$$\overline{M}_{\rm n}^2 = \frac{M^2(1+p)}{(1-p)^2} \text{ [Problem 23.13]}$$

Therefore, $\dfrac{\overline{M}_{\rm n}^3}{\overline{M}_{\rm n}^2} = \boxed{\dfrac{M(1+4p+p^2)}{1-p^2}}$

(b) $\langle n\rangle = \dfrac{1}{1-p}$ [23.8], so $p = 1 - \dfrac{1}{\langle n\rangle}$

$$\frac{\overline{M}_{\rm n}^3}{\overline{M}_{\rm n}^2} = \boxed{(6\langle n\rangle^2 - 6\langle n\rangle + 1)\langle n\rangle}$$

P23.16 $\dfrac{d[A]}{dt} = -k[A]^2[OH] = -k[A]^3$ because $[A] = [OH]$.

$$\frac{d[A]}{[A]^3} = -k\,dt \quad \text{and} \quad \int_{[A]_0}^{[A]}\frac{d[A]}{[A]^3} = -k\int_0^t dt = -kt$$

Since $\displaystyle\int\frac{dx}{x^3} = \frac{-1}{2x^2}$, the equation becomes

$$\frac{1}{[A]^2} - \frac{1}{[A]_0^2} = 2kt \quad \text{or} \quad [A] = [A]_0(1+2kt[A]_0)^{-1/2}$$

By eqn 23.8a the degree of polymerization, $\langle n\rangle$, is given by

$$\langle n\rangle = \frac{[A]_0}{[A]} = \boxed{(1+2kt[A]_0)^{1/2}}$$

P23.18 $A \rightarrow B \quad \dfrac{d[B]}{dt} = I_a$

$B \rightarrow A \quad \dfrac{d[B]}{dt} = -k[B]^2$

In the photostationary state $I_a - k[B]^2 = 0$. Hence,

$$[B] = \boxed{\left(\frac{I_a}{k}\right)^{1/2}} \propto [A]^{1/2} \quad [\text{because } I \propto [A]]$$

The illumination may increase the rate of the forward reaction without affecting the reverse reaction. Hence the position of equilibrium may be shifted toward products.

P23.20

$$Cl_2 + h\nu \rightarrow 2Cl \qquad I_a$$
$$Cl + CHCl_3 \rightarrow CCl_3 + HCl \qquad k_2$$
$$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl \qquad k_3$$
$$2CCl_3 + Cl_2 \rightarrow 2CCl_4 \qquad k_4$$

(i) $\dfrac{d[CCl_4]}{dt} = 2k_4[CCl_3]^2[Cl_2] + k_3[CCl_3][Cl_2]$

(ii) $\dfrac{d[CCl_3]}{dt} = k_2[Cl][CHCl_3] - k_3[CCl_3][Cl_2] - 2k_4[CCl_3]^2[Cl_2] = 0$

(iii) $\dfrac{d[Cl]}{dt} = 2I_a - k_2[Cl][CHCl_3] + k_3[CCl_3][Cl_2] = 0$

(iv) $\dfrac{d[Cl_2]}{dt} = -I_a - k_3[CCl_3][Cl_2] - k_4[CCl_3]^2[Cl_2]$

Therefore, $I_a = k_4[CCl_3]^2[Cl_2]$ [(ii) + (iii)]

which implies that

$$[CCl_3] = \left(\frac{1}{k_4}\right)^{1/2}\left(\frac{I_a}{[Cl_2]}\right)^{1/2}$$

Then, with (i),

$$\frac{d[CCl_4]}{dt} = 2I_a + \frac{k_3 I_a^{1/2}[Cl]^{1/2}}{k_4^{1/2}}$$

When the pressure of chlorine is high, and the initiation rate is slow (in the sense that the lowest powers of I_a dominate), the second term dominates the first, giving

$$\frac{d[CCl_4]}{dt} = \frac{k_3 I_a^{1/2}}{k_4^{1/2}}[Cl_2]^{1/2} = \boxed{kI_a^{1/2}[Cl_2]^{1/2}}$$

with $k = k_3/k_4^{1/2}$. It seems necessary to suppose that Cl + Cl recombination (which needs a third body) is unimportant.

Solutions to applications

P23.22 The rate equation is

$$\frac{dN}{dt} = bN - dN$$

which has the solution

$$\boxed{N(t) = N_0 e^{(b-d)t} = N_0 e^{kt}}$$

A least squares fit to the above data gives

$N_0 = 0.484 \times 10^9 \approx 0.5 \times 10^9$

$k = 9.19 \times 10^{-3}\,y^{-1}$

R^2 = (coefficient of determination) = 0.983

Standard error of estimate $= 0.130 \times 10^9$

Thus, this model of population growth for the planet as a whole fits the data fairly well.

COMMENT. Despite the fact that the Malthusian model seems to fit the (admittedly crude) population data it has been much criticized. An alternative rate equation that takes into amount the carrying capacity K of the planet is due to Verhulst (1836). This rate equation is

$$\frac{dN}{dt} = kN\left(1 - \frac{N}{k}\right)$$

Question. Does the Verhulst model fit our limited data any better?

P23.24 We draw up the table below, which includes data rows required for a Lineweaver–Burk plot ($1/v$ against $1/[S]_0$). The linear regression fit is found for the plot. See Figure 23.4

$[ATP]/(\mu mol\,dm^{-3})$	0.60	0.80	1.4	2.0	3.0
$v/(\mu mol\,dm^{-3}\,s^{-1})$	0.81	0.97	1.30	1.47	1.69
$1/\{[ATP]/(\mu mol\,dm^{-3})\}$	1.67	1.25	0.714	0.500	0.333
$1/\{v/(\mu mol\,dm^{-3}\,s^{-1})\}$	1.23	1.03	0.769	0.680	0.592

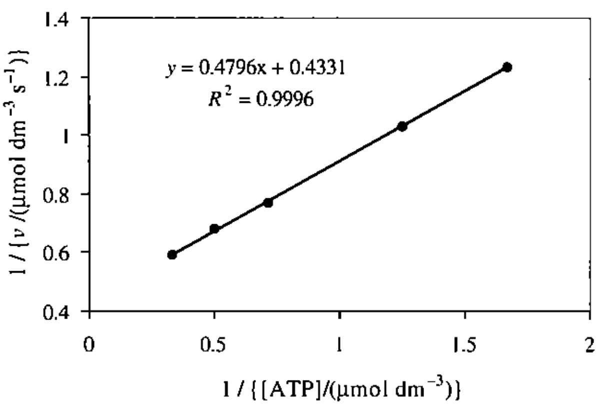


Figure 23.4

$1/v_{max} = \text{intercept}$ [23.22]

$v_{max} = 1/\text{intercept} = 1/(0.433\,\mu mol\,dm^{-3}\,s^{-1}) = \boxed{2.31\,\mu mol\,dm^{-3}\,s^{-1}}$

$k_b = v_{max}\,/\,[E]_0$ [23.20*b*] $= (2.31\,\mu mol\,dm^{-3}\,s^{-1})\,/\,(0.020\,\mu mol\,dm^{-3}) = \boxed{115\,s^{-1}}$

$k_{cat} = k_b$ [23.23] $= \boxed{115\,s^{-1}}$

$K_M = v_{max} \times \text{slope}$ [23.22] $= (2.31\,\mu mol\,dm^{-3}\,s^{-1}) \times (0.480\,s) = \boxed{1.11\,\mu mol\,dm^{-3}}$

$\varepsilon = k_{cat}\,/\,K_M$ [23.24] $= (115\,s^{-1})\,/\,(1.11\,\mu mol\,dm^{-3}) = \boxed{104\,dm^3\mu mol^{-1}\,s^{-1}}$

P23.26 (a) The dissociation equilibrium may be rearranged to give the following relationships.

$$[E^-] = K_{E,a}[EH]/[H^+] \quad [EH_2^+] = [EH][H^+]/K_{E,b}$$
$$[ES^-] = K_{ES,a}[ESH]/[H^+] \quad [ESH_2] = [ESH][H^+]/K_{ES,b}$$

Mass balance provides an equation for [EH].

$$[E]_0 = [E^-] + [EH] + [EH_2^+] + [ES^-] + [ESH] + [ESH_2]$$
$$= \frac{K_{E,a}[EH]}{[H^+]} + [EH] + \frac{[EH][H^+]}{K_{E,b}} + \frac{K_{ES,a}[ESH]}{[H^+]} + [ESH] + \frac{[ESH][H^+]}{K_{ES,b}}$$
$$[EH] = \frac{[E]_0 - \{1 + ([H^+]/K_{ES,b}) + (K_{ES,a}/[H^+])\}[ESH]}{1 + ([H^+]/K_{E,b}) + (K_{E,a}/[H^+])}$$
$$= \frac{[E]_0 - c_1[ESH]}{c_2}$$

The steady-state approximation provides an equation for [ESH],

$$\frac{d[ESH]}{dt} k_a[EH][S] - k_a'[ESH] - k_b[ESH] = 0$$
$$[ESH] = \frac{k_a}{k_a' + k_b}[EH][S] = k_M^{-1}[EH][S]$$
$$= k_M^{-1}[S]\left\{\frac{[E]_0 - c_1[ESH]}{c_2}\right\}$$
$$[ESH] = \frac{K_M^{-1}[S][E]_0/c_2}{1 + (k_M^{-1}[S]c_1/c_2)} = \frac{[E]_0/c_1}{1 + (k_M(c_2/c_1)/[S])}$$

The rate law becomes:

$$v = d[P]/dt = k_b[ESH]$$
$$v = \frac{v'_{max}}{1 + k'_M/[S]}$$

where $v'_{max} = \dfrac{k_b[E]_0}{\{1 + ([H^+]/K_{ES,b}) + (K_{ES,a}/[H^+])\}}$

$$K'_M = \left\{\frac{1 + ([H^+]/K_{E,b}) + (K_{E,a}/[H^+])}{1 + ([H^+]/K_{ES,b}) + (K_{ES,a}/[H^+])}\right\}$$

(b) $v_{max} = 1.0 \times 10^{-6}\,mol\,dm^{-3}\,s^{-1}$

$K_{ES,b} = 1.0 \times 10^{-6}\,mol\,dm^{-3}$

$K_{ES,a} = 1.0 \times 10^{-8}\,mol\,dm^{-3}$

The graph (Figure 23.5a) indicates a maximum value of v'_{max} at pH = 7.0 for this set of equilibrium and kinetic constants. A formula for the pH of the maximum can be derived by finding the point at

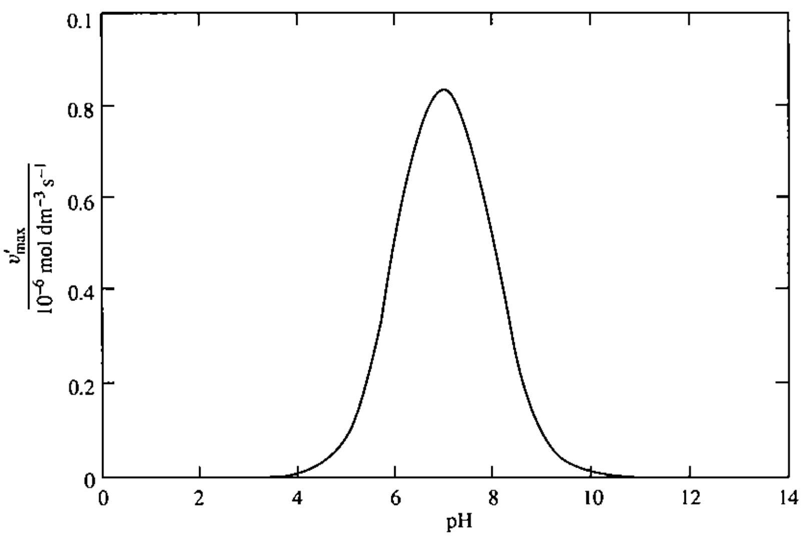


Figure 23.5(a)

which $\frac{dv'_{max}}{d[H^+]} = 0$. This gives:

$$[H^+]_{max} = (K_{ES,a}K_{ES,b})^{1/2}$$

Inserting constants, $[H^+]_{max} = \sqrt{(1.0 \times 10^{-8} mol\,dm^{-3})(1.0 \times 10^{-6} mol\,dm^{-3})}$
$= 1.0 \times 10^{-7} mol\,dm^{-3}$

which corresponds to $\boxed{pH = 7.0}$

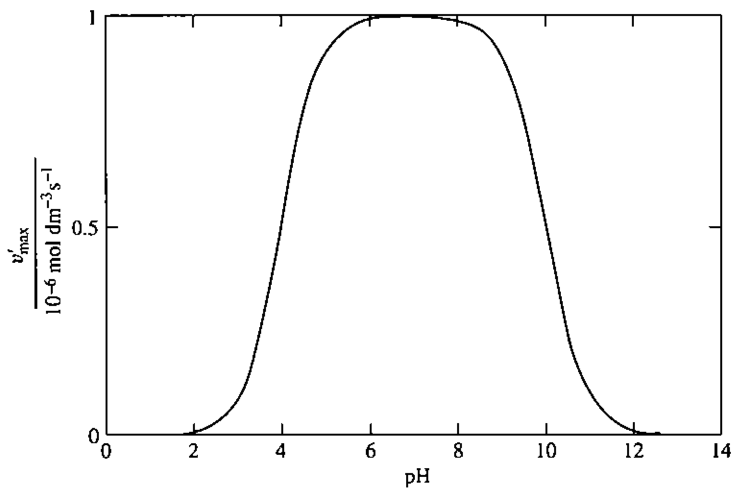


Figure 23.5(b)

(c) $v_{max} = 1.0 \times 10^{-6}\,\text{mol dm}^{-3}\text{s}^{-1}$

$K_{ES,b} = 1.0 \times 10^{-4}\,\text{mol dm}^{-3}$

$K_{ES,a} = 1.0 \times 10^{-10}\,\text{mol dm}^{-3}$

The constants of part (c) give a much broader curve (Figure 23.5b) than do the constants of part (b). This reflects the behavior of the term $1 + [H^+]/K_{ES,b} + K_{ES,a}/[H^+]$ in the denominator of the v'_{max} expression. When $K_{ES,b}$ is relatively large, large $[H^+]$ values (low pH) cause growth in the values of v'_{max}. However, when $K_{ES,a}$ is relatively small, very small $[H^+]$ values (high pH) cause a decline in the v'_{max} values.

P23.28 The description of the progress of infectious diseases can be represented by the mechanism

$$\text{S} \rightarrow \text{I} \rightarrow \text{R}$$

Only the $\boxed{\text{first step is autocatalytic}}$ as indicated in the first rate expression. If the three rate equations are added

$$\frac{d\text{S}}{dt} + \frac{d\text{I}}{dt} + \frac{d\text{R}}{dt} = 0$$

and, hence there is no change with time of the total population, that is

$$\text{S}(t) + \text{I}(t) + \text{R}(t) = N$$

Whether the infection spreads or dies out is determined by

$$\frac{d\text{I}}{dt} = r\text{SI} - a\text{I}$$

At $t = 0, \text{I} = \text{I}(0) = \text{I}_0$. Since the process is autocatalytic $\text{I}(0) \neq 0$.

$$\left(\frac{d\text{I}}{dt}\right)_{t=0} = \text{I}_0\,(r\text{S}_0 - a)$$

If $a > r\text{S}_0 \left(\frac{d\text{I}}{dt}\right)_{t=0} < 0$, and the infection dies out. If $a < r\text{S}, \left(\frac{d\text{I}}{dt}\right)_{t=0} > 0$ and the infection spreads (an epidemic). Thus

$$\boxed{\frac{a}{r} < \text{S}_0}\ \text{[infection spreads]}$$

$$\boxed{\frac{a}{r} > \text{S}_0}\ \text{[infection dies out]}$$

P23.30

$$\underset{\text{Chlorophyll}}{\text{C}} + \underset{\text{Quinone}}{\text{Q}} \xrightarrow{h\nu} \text{C}^* + \text{Q} \xrightarrow{\text{electrontransfer}} \text{C}^+ + \text{Q}^-$$

Direct electron transfer from the ground state of C is not spontaneous. It is spontaneous from the excited state. The difference between the ΔG's of the two processes is given by the expression:

$$\Delta(\Delta G) = \Delta G_{C^*} - \Delta G_C \approx U_C - U_{C^*} \approx -(U_{\text{LUMO}} - U_{\text{HOMO}})$$

where $U_{\rm LUMO}$ and $U_{\rm HOMO}$ are energies of the LUMO and HOMO of chlorophyll. Since $\Delta\Delta G < 0$, we see that electron transfer is exergonic and spontaneous when the electron is transferred from the excited state of chlorophyll.

P23.32 The rate of reaction is the rate at which ozone absorbs photons times the quantum yield. The rate at which ozone absorbs photons is the rate at which photons impinge on the ozone times the fraction of photons absorbed. That fraction is $1 - T$, where T is the transmittance. T is related to the absorbance A by

$$A = -\log T = \varepsilon c l \quad \text{so} \quad 1 - T = 1 - 10^{-\varepsilon c l}$$

$$1 - T = 1 - 10^{\{(260\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}})\times(8\times10^{-9}\,\mathrm{mol\,dm^{-3}})\times(10^5\,\mathrm{cm})} = 0.38$$

If we let F stand for the flux of photons (the rate at which photons impinge on our sample of ozone), then the rate of reaction is

$$v = \phi(1 - T)F = (0.94) \times (0.38) \times \frac{(1 \times 10^{14}\,\mathrm{cm^{-2}\,s^{-1}}) \times (1000\,\mathrm{cm^3\,dm^{-3}})}{(6.022 \times 10^{23}\,\mathrm{mol^{-1}}) \times (10^5\,\mathrm{cm})}$$

$$= \boxed{5.9 \times 10^{-13}\,\mathrm{mol\,dm^{-3}s^{-1}}}$$

P23.34 The rate of reaction for this reaction is

$$v = k[\mathrm{Cl}][\mathrm{O_3}]$$

(a) $v = (1.7 \times 10^{10}\mathrm{dm^3mol^{-1}s^{-1}})\exp(-260\,\mathrm{K}/220\,\mathrm{K}) \times (5 \times 10^{-17}\,\mathrm{mol\,dm^{-3}})$

$\times\ (8 \times 10^{-9}\,\mathrm{mol\,dm^{-3}})$

$= \boxed{2.\bar{1} \times 10^{-15}\,\mathrm{mol\,dm^{-3}\,s^{-1}}}$

(b) $v = (1.7 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}s^{-1}})\exp(-260\,\mathrm{K}/270\,\mathrm{K}) \times (3 \times 10^{-15}\,\mathrm{mol\,dm^{-3}})$

$\times\ (8 \times 10^{-11}\,\mathrm{mol\,dm^{-3}})$

$= \boxed{1.\bar{6} \times 10^{-15}\,\mathrm{mol\,dm^{-3}\,s^{-1}}}$

24 Molecular reaction dynamics

Answers to discussion questions

D24.2 A reaction in solution can be regarded as the outcome of two stages: one is the encounter of two reactant species; this is followed by their reaction in the second stage, if they acquire their activation energy. If the rate-determining step is the former, then the reaction is said to be diffusion-controlled. If the rate-determining step is the latter, then the reaction is activation controlled. For a reaction of the form $A + B \rightarrow P$ that obeys the second-order rate law $v = k_2[A][B]$, in the diffusion-controlled regime,

$$k_2 = 4\pi R^* D N_A$$

where D is the sum of the diffusion coefficients of the two reactant species and R^* is the distance at which reaction occurs. A further approximation is that each molecule obeys the Stokes–Einstein relation and Stokes' law, and then

$$k_2 \approx \frac{8RT}{3\eta}$$

where η is the viscosity of the medium. The result suggests that k_2 is independent of the radii of the reactants.

D24.4 In the kinetic salt effect, the rate of a reaction in solution is changed by modification of the ionic strength of the medium. If the reactant ions have the same sign of charge (as in cation/cation or anion/anion reactions), then an increase in ionic strength increases the rate constant. If the reactant ions have opposite signs (as in cation/anion reactions), then an increase in ionic strength decreases the rate constant. In the former case, the effect can be traced to the denser ionic atmosphere (see the Debye–Huckel theory) that forms round the newly formed and highly charged ion that constitutes the activated complex and the stronger interaction of that ion with the atmosphere. In the latter case, the ion corresponding to the activated complex has a lower charge than the reactants and hence it has a more diffuse ionic atmosphere and interacts with it more weakly. In the limit of low ionic strength the rate constant can be expected to follow the relation

$$\log k = \log k^\circ + 2Az_A z_B I^{1/2}$$

D24.6 Refer to Figures 24.21 and 24.22 of the text. The first of these figures shows an attractive potential energy surface, the second, a repulsive surface.

(a) Consider Figure 24.21. If the original molecule is vibrationally excited, then a collision with an incoming molecule takes the system along the floor of the potential energy valley (trajectory C). This path is bottled up in the region of the reactants, and does not take the system to the saddle point.

If, however, the same amount of energy is present solely as translational kinetic energy, then the system moves along a successful encounter trajectory C* and travels smoothly over the saddle point into products. We can therefore conclude that reactions with attractive potential energy surfaces proceed more efficiently if the energy is in relative translational motion. Moreover, the potential surface shows that once past the saddle point the trajectory runs up the steep wall of the product valley, and then rolls from side to side as it falls to the foot of the valley as the products separate. In other words, the products emerge in a vibrationally excited state.

(b) Now consider the repulsive surface (Figure 24.22). On trajectory C the collisional energy is largely in translation. As the reactants approach, the potential energy rises. Their path takes them up the opposing face of the valley, and they are reflected back into the reactant region. This path corresponds to an unsuccessful encounter, even though the energy is sufficient for reaction. On a successful trajectory C*, some of the energy is in the vibration of the reactant molecule and the motion causes the trajectory to weave from side to side up the valley as it approaches the saddle point. This motion may be sufficient to tip the system round the corner to the saddle point and then on to products. In this case, the product molecule is expected to be in an unexcited vibrational state. Reactions with repulsive potential surfaces can therefore be expected to proceed more efficiently if the excess is present as vibrations.

D24.8 Donor (D) and acceptor (A) must collide before they can react. Consequently, the rate of their reaction in solution is initially determined by the rate of diffusion of the reacting species. After D and A have arrived at the critical reaction distance r^* (comparable to r, the edge-to-edge distance), the rate constant for electron transfer is a function of two factors. See Sections 24.11(a) and (b) and eqn 24.81. The first is the tunneling rate of the electron through an energy barrier that is a function of the ionization energies of the complexes DA and D^+A^-. The second is the Gibbs energy of activation.

Effective transfer can occur only when the electronic energies in the two complexes match. The electronic energies are a function of the internuclear separations in DA and D^+A^- as illustrated in Figures 24.27 and 24.28; therefore, the distance between D and A plays a critical role in determining the rate of electron transfer. The tunneling rate is determined by the matrix element of the coupling term in the Hamiltonian which exhibits an exponential dependence on the negative of r, as given by eqn 24.80.

Further Information 24.1 shows how the Gibbs energy of activation is related to the reorganization energy associated with molecular rearrangements which include the relative reorientation of the D and A molecules and the relative reorientation of the solvent molecules surrounding DA.

Solutions to exercises

E24.1(b) The collision frequency is

$$z = \frac{2^{1/2}\sigma\,\langle\bar{c}\rangle\,p}{kT} \quad \text{where } \sigma = \pi d^2 = 4\pi r^2 \text{ and } \langle\bar{c}\rangle = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\text{so } z = \frac{2^{1/2}p}{kT}(4\pi r^2)\left(\frac{8RT}{\pi M}\right)^{1/2} = \frac{16pN_A r^2\pi^{1/2}}{(RTM)^{1/2}}$$

$$= \frac{16\times(100\times10^3\,\text{Pa})\times(6.022\times10^{23}\,\text{mol}^{-1})\times(180\times10^{-12}\,\text{m})^2\times(\pi)^{1/2}}{[(8.3145\,\text{J K}^{-1}\text{mol}^{-1})\times(298\,\text{K})\times(28.01\times10^{-3}\,\text{kg mol}^{-1})]^{1/2}}$$

$$= \boxed{6.64\times10^9\,\text{s}^{-1}}$$

The collision density is

$$Z_{AA} = \frac{1}{2}zN/V = \frac{zp}{2kT} = \frac{(6.64 \times 10^9\,\mathrm{s^{-1}}) \times (100 \times 10^3\,\mathrm{Pa})}{2(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}) \times (298\,\mathrm{K})} = \boxed{8.07 \times 10^{34}\,\mathrm{m^{-3}s^{-1}}}$$

Raising the temperature at constant volume means raising the pressure in proportion to the temperature

$$Z_{AA} \propto \sqrt{T}$$

so the percent increase in z and Z_{AA} due to a 10 K increase in temperature is $\boxed{1.6\text{ percent}}$, same as Exercise 24.1(a).

E24.2(b) The appropriate fraction is given by

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

The values in question are

(a) (i) $f = \exp\left(\dfrac{-15 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}\right) = \boxed{2.4 \times 10^{-3}}$

(ii) $f = \exp\left(\dfrac{-15 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (800\,\mathrm{K})}\right) = \boxed{0.10}$

(b) (i) $f = \exp\left(\dfrac{-150 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (300\,\mathrm{K})}\right) = \boxed{7.7 \times 10^{-27}}$

(ii) $f = \exp\left(\dfrac{-150 \times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (800\,\mathrm{K})}\right) = \boxed{1.6 \times 10^{-10}}$

E24.3(b) A straightforward approach would be to compute $f = \exp(-E_a/RT)$ at the new temperature and compare it to that at the old temperature. An approximate approach would be to note that f changes from $f_0 = \exp(-E_a/RT)$ to $f = \exp(-E_a/RT(1+x))$, where x is the fractional increase in the temperature. If x is small, the exponent changes from $-E_a/RT$ to approximately $(-E_a/RT)(1-x)$ and f changes from $\exp(-E_a/RT)$ to $\exp(-E_a(1-x)/RT) = \exp(-E_a/RT)\left[\exp(-E_a/RT)\right]^{-x} = f_0 f_0^{-x}$. Thus the new Boltzmann factor is the old one times a factor of f_0^{-x}. The factor of increase is

(a) (i) $f_0^{-x} = (2.4 \times 10^{-3})^{-10/300} = \boxed{1.2}$

(ii) $f_0^{-x} = (0.10)^{-10/800} = \boxed{1.03}$

(b) (i) $f_0^{-x} = (7.7 \times 10^{-27})^{-10/300} = \boxed{7.4}$

(ii) $f_0^{-x} = (1.6 \times 10^{-10})^{-10/800} = \boxed{1.3}$

E24.4(b) The reaction rate is given by

$$v = P\sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT)[D_2][Br_2]$$

so, in the absence of any estimate of the reaction probability P, the rate constant is

$$k = \sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT)$$

$$= [0.30 \times (10^{-9}\,\text{m})^2] \times \left(\frac{8(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (450\,\text{K})}{\pi(3.930\,\text{u}) \times (1.66 \times 10^{-27}\,\text{kg u}^{-1})}\right)^{1/2}$$

$$\times (6.022 \times 10^{23}\,\text{mol}^{-1}) \exp\left(\frac{-200 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (450\,\text{K})}\right)$$

$$= 1.71 \times 10^{-15}\,\text{m}^3\,\text{mol}^{-1}\text{s}^{-1} = \boxed{1.7 \times 10^{12}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

E24.5(b) The rate constant is

$$k_d = 4\pi R^* D N_A$$

where D is the sum of two diffusion constants. So

$$k_d = 4\pi(0.50 \times 10^{-9}\,\text{m}) \times (2 \times 4.2 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})$$

$$= \boxed{3.2 \times 10^7\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

In more common units, this is

$$k_d = \boxed{3.2 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

E24.6(b) **(a)** A diffusion-controlled rate constant in decylbenzene is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{3 \times (3.36 \times 10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})} = \boxed{1.97 \times 10^6\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

(b) In concentrated sulfuric acid

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{3 \times (27 \times 10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})} = \boxed{2.4 \times 10^5\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

E24.7(b) The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{3 \times (0.601 \times 10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})} = \boxed{1.10 \times 10^7\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

In more common units, $k_d = \boxed{1.10 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$

The recombination reaction has a rate of

$$v = k_d[\text{A}][\text{B}] \qquad \text{with } [\text{A}] = [\text{B}]$$

so the half-life is given by

$$t_{1/2} = \frac{1}{k[\text{A}]_0} = \frac{1}{(1.10 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) \times (1.8 \times 10^{-3}\,\text{mol dm}^{-3})} = \boxed{5.05 \times 10^{-8}\,\text{s}}$$

E24.8(b) The reactive cross-section σ^* is related to the collision cross-section σ by

$$\sigma^* = P\sigma \quad \text{so} \quad P = \sigma^*/\sigma.$$

The collision cross-section σ is related to effective molecular diameters by

$$\sigma = \pi d^2 \quad \text{so} \quad d = (\sigma/\pi)^{1/2}$$

Now $\sigma_{AB} = \pi d_{AB}^2 = \pi\left[\frac{1}{2}(d_A + d_B)\right]^2 = \frac{1}{4}\left(\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2}\right)^2$

$$\text{so} \quad P = \frac{\sigma^*}{\frac{1}{4}\left(\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2}\right)^2}$$

$$= \frac{8.7 \times 10^{-22}\,\text{m}}{\frac{1}{4}[((0.88)^{1/2} + (0.40)^{1/2}) \times 10^{-9}\,\text{m}]^2} = \boxed{1.41 \times 10^{-3}}$$

E24.9(b) The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (293\,\text{K})}{3 \times (1.27 \times 10^{-3}\,\text{kg m}^{-1}\,\text{s}^{-1})} = 5.12 \times 10^6\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

In more common units, $k_d = 5.12 \times 10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$.

The recombination reaction has a rate of

$$v = k_d[\text{A}][\text{B}] = (5.12 \times 10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) \times (0.200\,\text{mol dm}^{-3}) \times (0.150\,\text{mol dm}^{-3})$$

$$= \boxed{1.54 \times 10^8\,\text{mol dm}^{-3}\,\text{s}^{-1}}$$

E24.10(b) The enthalpy of activation for a reaction in solution is

$$\Delta^{\ddagger}H = E_a - RT = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (6134\,\text{K}) - (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})$$

$$= 4.852 \times 10^4\,\text{J mol}^{-1} = \boxed{48.52\,\text{kJ mol}^{-1}}$$

The entropy of activation is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}}$$

$$B = \frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})^2}{(6.626 \times 10^{-34}\,\text{J s}) \times (1.00 \times 10^5\,\text{Pa})}$$

$$= 1.54 \times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

$$\text{so } \Delta^{\ddagger}S = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\ln\frac{8.72 \times 10^{12}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}{(1000\,\text{dm}^3\,\text{m}^{-3}) \times (1.54 \times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1})} - 1\right)$$

$$= \boxed{-32.2\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

COMMENT. In this connection, the enthalpy of activation is often referred to as "energy" of activation.

E24.11(b) The Gibbs energy of activation is related to the rate constant by

$$k_2 = B\exp\left(\frac{-\Delta^{\ddagger}G}{RT}\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}} \quad \text{so} \quad \Delta^{\ddagger}G = -RT\ln\frac{k_2}{B}$$

$$k_2 = (6.45\times10^{13}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}})\mathrm{e}^{-\{(5375\,\mathrm{K})/(298\,\mathrm{K})\}} = 9.47\times10^{5}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$$
$$= 947\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

Using the value of B computed in Exercise 27.13(b), we obtain

$$\Delta^{\ddagger}G = -(8.3145\times10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\times(298\,\mathrm{K})\times\ln\left(\frac{947\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}{1.54\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}\right)$$
$$= \boxed{46.8\,\mathrm{kJ\,mol^{-1}}}$$

E24.12(b) The entropy of activation for a bimolecular reaction in the gas phase is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 2\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}}$$
$$B = \frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times[(55+273)\,\mathrm{K}]^2}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(1.00\times10^{5}\,\mathrm{Pa})}$$
$$= 1.86\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

The rate constant is

$$k_2 = A\exp\left(\frac{-E_{\mathrm{a}}}{RT}\right) \quad \text{so} \quad A = k_2\exp\left(\frac{E_{\mathrm{a}}}{RT}\right)$$
$$A = (0.23\,\mathrm{m^3\,mol^{-1}\,s^{-1}})\times\exp\left(\frac{49.6\times10^{3}\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(328\,\mathrm{K})}\right)$$
$$= 1.8\times10^{7}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$$

and $\Delta^{\ddagger}S = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times\left(\ln\left(\dfrac{1.8\times10^{7}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}{1.86\times10^{11}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}\right) - 2\right)$

$$= \boxed{-93\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

E24.13(b) The entropy of activation for a bimolecular reaction in the gas phase is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 2\right) \quad \text{where } B = \frac{kRT^2}{hp^{\ominus}}$$

For the collision of structureless particles, the rate constant is

$$k_2 = N_{\mathrm{A}}\left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma\exp\left(\frac{-\Delta E_0}{RT}\right)$$

so the prefactor is

$$A = N_A\left(\frac{8kT}{\pi\mu}\right)^{1/2}\sigma = 4N_A\left(\frac{RT}{\pi M}\right)^{1/2}\sigma$$

where we have used the fact that $\mu = \frac{1}{2}m$ for identical particles and $k/m = R/M$. So

$$A = 4 \times (6.022 \times 10^{23}\,\text{mol}^{-1}) \times \left(\frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{\pi \times (78 \times 10^{-3}\,\text{kg mol}^{-1})}\right)^{1/2} \times (0.68 \times 10^{-18}\,\text{m}^2)$$

$$= 2.13 \times 10^8\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

$$B = \frac{(1.381 \times 10^{-23}\,\text{J K}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})^2}{(6.626 \times 10^{-34}\,\text{J s}) \times (1.00 \times 10^5\,\text{Pa})}$$

$$= 4.33 \times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$$

and $\Delta^{\ddagger}S = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\ln\left(\frac{2.13 \times 10^8\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}{4.33 \times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}}\right) - 2\right)$

$$= \boxed{-80.0\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

E24.14(b) (a) The entropy of activation for a unimolecular gas-phase reaction is

$$\Delta^{\ddagger}S = R\left(\ln\frac{A}{B} - 1\right) \quad \text{where } B = 1.54 \times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1} \text{ [See Exercise 24.14(a)]}$$

so $\Delta^{\ddagger}S = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})$

$$\times \left(\ln\left(\frac{2.3 \times 10^{13}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}{(1000\,\text{dm}^3\,\text{m}^{-3}) \times (1.54 \times 10^{11}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1})}\right) - 1\right)$$

$$= \boxed{-24.1\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

(b) The enthalpy of activation is

$$\Delta^{\ddagger}H = E_a - RT = 30.0 \times 10^3\,\text{J mol}^{-1} - (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})$$

$$= 27.5 \times 10^3\,\text{J mol}^{-1} = \boxed{27.5\,\text{kJ mol}^{-1}}$$

(c) The Gibbs energy of activation is

$$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 27.5\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (-24.1 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1})$$

$$= \boxed{34.7\,\text{kJ mol}^{-1}}$$

E24.15(b) The dependence of a rate constant on ionic strength is given by

$$\log k_2 = \log k_2^{\circ} + 2Az_Az_BI^{1/2}$$

At infinite dilution, $I = 0$ and $k_2 = k_2^\circ$, so we must find

$$\log k_2^\circ = \log k_2 - 2Az_Az_BI^{1/2} = \log(1.55) - 2 \times (0.509) \times (+1) \times (+1) \times (0.0241)^{1/2}$$

$$= 0.0323 \quad \text{and} \quad \boxed{k_2^\circ = 1.08\,\text{dm}^6\,\text{mol}^{-2}\text{min}^{-1}}$$

E24.16(b) Equation 24.84 holds for a donor–acceptor pair separated by a constant distance, assuming that the reorganization energy is constant:

$$\ln k_{\text{et}} = -\frac{(\Delta_r G^\ominus)^2}{4\lambda RT} - \frac{\Delta_r G^\ominus}{2RT} + \text{constant},$$

or equivalently

$$\ln k_{\text{et}} = -\frac{(\Delta_r G^\ominus)^2}{4\lambda kT} - \frac{\Delta_r G^\ominus}{2kT} + \text{constant},$$

if energies are expressed as molecular rather than molar quantities. Two sets of rate constants and reaction Gibbs energies can be used to generate two equations (eqn 24.84 applied to the two sets) in two unknowns: λ and the constant.

$$\ln k_{\text{et},1} + \frac{(\Delta_r G_1^\ominus)^2}{4\lambda kT} + \frac{\Delta_r G_1^\ominus}{2kT} = \text{constant} = \ln k_{\text{et},2} + \frac{(\Delta_r G_2^\ominus)^2}{4\lambda kT} + \frac{\Delta_r G_2^\ominus}{2kT},$$

$$\text{so} \quad \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{\Delta\lambda kT} = \ln\frac{k_{\text{et},2}}{k_{\text{et},1}} + \frac{\Delta_r G_2^\ominus - \Delta_r G_1^\ominus}{2kT}$$

$$\text{and } \lambda = \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{4\left(kT\ln(k_{\text{et},2}/k_{\text{et},1}) + (\Delta_r G_2^\ominus - \Delta_r G_1^\ominus/2)\right)}$$

$$\lambda = \frac{(-0.665\,\text{eV})^2 - (-0.975\,\text{eV})^2}{\dfrac{4(1.381 \times 10^{-23}\,\text{J K}^{-1})(298\,\text{K})}{1.602 \times 10^{-19}\,\text{J eV}^{-1}}\ln\dfrac{3.33 \times 10^6}{2.02 \times 10^5} - 2(0.975 - 0.665)\,\text{eV}} = \boxed{1.53\bar{1}\,\text{eV}}$$

If we knew the activation Gibbs energy, we could use eqn 24.81 to compute $\langle H_{DA}\rangle$ from either rate constant, and we *can* compute the activation Gibbs energy from eqn 24.82:

$$\Delta^\ddagger G = \frac{(\Delta_r G^\ominus + \lambda)^2}{4\lambda} = \frac{[(-0.665 + 1.53\bar{1})\,\text{eV}]^2}{4(1.53\bar{1}\,\text{eV})} = 0.122\,\text{eV}.$$

$$\text{Now } k_{\text{et}} = \frac{2\,\langle H_{DA}\rangle^2}{h}\left(\frac{\pi^3}{4\lambda kT}\right)^{1/2}\exp\left(\frac{-\Delta^\ddagger G}{kT}\right)$$

so $\langle H_{DA}\rangle = \left(\dfrac{hk_{et}}{2}\right)^{1/2}\left(\dfrac{4\lambda kT}{\pi^3}\right)^{1/4}\exp\left(\dfrac{\Delta^{\ddagger}G}{2kT}\right)$,

$$\langle H_{DA}\rangle = \left(\frac{(6.626\times10^{-34}\,\mathrm{J\,s})(2.02\times10^{5}\,\mathrm{s^{-1}})}{2}\right)^{1/2}$$
$$\times\left(\frac{4(1.53\bar{1}\,\mathrm{eV})(1.602\times10^{-19}\,\mathrm{J\,eV^{-1}})(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})}{\pi^3}\right)^{1/4}$$
$$\times\exp\left(\frac{(0.122\,\mathrm{eV})(1.602\times10^{-19}\,\mathrm{J\,eV^{-1}})}{2(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})}\right) = \boxed{9.39\times10^{-24}\,\mathrm{J}}$$

E24.17(b) Equation 24.83 applies. In Exercise 24.17(a), we found the parameter β to equal $12\,\mathrm{nm^{-1}}$, so:

$$\ln k_{et}/\mathrm{s^{-1}} = -\beta r + \text{constant} \quad \text{so} \quad \text{constant} = \ln k_{et}/\mathrm{s^{-1}} + \beta r,$$

and constant $= \ln 2.02\times10^{5} + (12\,\mathrm{nm^{-1}})(1.11\,\mathrm{nm}) = 25$.

Taking the exponential of eqn 24.83 yields:

$$k_{et} = \mathrm{e}^{-\beta r+\text{constant}}\,\mathrm{s^{-1}} = \mathrm{e}^{-(12/\mathrm{nm})(1.48\,\mathrm{nm})+25}\,\mathrm{s^{-1}} = \boxed{1.4\times10^{3}\,\mathrm{s^{-1}}}.$$

Solutions to problems

Solutions to numerical problems

P24.2 Draw up the following table as the basis of an Arrhenius plot

T/K	600	700	800	1000
$10^3\,\mathrm{K}/T$	1.67	1.43	1.25	1.00
$k/(\mathrm{cm^3\,mol^{-1}\,s^{-1}})$	4.6×10^{2}	9.7×10^{3}	1.3×10^{5}	3.1×10^{6}
$\ln(k/\mathrm{cm^3\,mol^{-1}\,s^{-1}})$	6.13	9.18	11.8	14.9

The points are plotted in Figure 24.1.

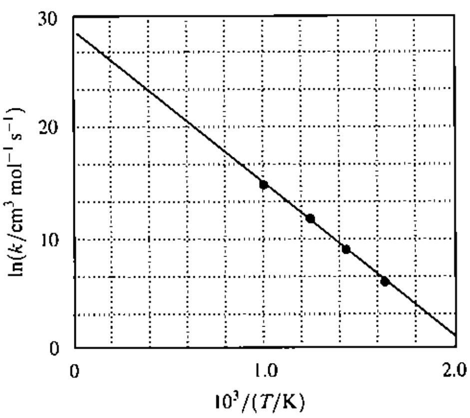


Figure 24.1

The least-squares intercept is at 28.3, which implies that

$$A/(\mathrm{cm^3\,mol^{-1}s^{-1}}) = e^{28.3} = 2.0 \times 10^{12}$$

From $A = N_A\sigma^*\left(\dfrac{8kT}{\pi\mu}\right)^{1/2}$ [Exercise 24.13(a)]

$$\sigma^* = \frac{A_{\text{exptl}}}{N_A(8kT/\pi\mu)^{1/2}} \quad \text{with } \mu = \frac{1}{2}m(\mathrm{NO_2})$$

$$= \left(\frac{A_{\text{exptl}}}{4N_A}\right)\left(\frac{\pi m}{kT}\right)^{1/2} = \left(\frac{2.0\times10^6\,\mathrm{m^3\,mol^{-1}\,s^{-1}}}{(4)\times(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)$$

$$\times\left(\frac{(\pi)\times(46\,\mathrm{u})\times(1.6605\times10^{-27}\,\mathrm{kg\,u^{-1}})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(750\,\mathrm{K})}\right)^{1/2}$$

$$= 4.0\times10^{-21}\,\mathrm{m^2} \quad \text{or} \quad \boxed{4.0\times10^{-3}\,\mathrm{nm^2}}$$

$$P = \frac{\sigma*}{\sigma} = \frac{4.0\times10^{-3}\,\mathrm{nm^2}}{0.60\,\mathrm{nm^2}} = \boxed{0.007}$$

P24.4 Draw up the following table for an Arrhenius Plot

$\theta/°\mathrm{C}$	-24.82	-20.73	-17.02	-13.00	-8.95
T/K	248.33	252.42	256.13	260.15	264.20
$10^3/(T/\mathrm{K})$	4.027	3.962	3.904	3.844	3.785
$\ln(k/\mathrm{s^{-1}})$	-9.01	-8.37	-7.73	-7.07	-6.55

The points are plotted in Figure 24.2.

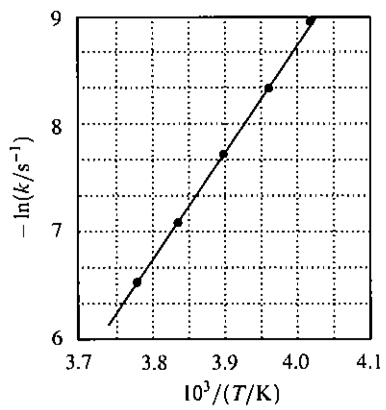


Figure 24.2

A least-squares fit of the data yields the intercept $+32.6$ at $1/T = 0$ and slope $-10.33 \times 10^3\,\mathrm{K}$. The former implies that $\ln(A/\mathrm{s^{-1}}) = 32.6$, and hence that $A = 1.4 \times 10^{14}\,\mathrm{s^{-1}}$. The slope yields $E_a/R = 10.33 \times 10^3\,\mathrm{K}$, and hence $E_a = \boxed{85.9\,\mathrm{kJ\,mol^{-1}}}$

In solution $\Delta^{\ddagger}H = E_a - RT$, so at $-20\,°C$

$$\Delta^{\ddagger}H = (85.9\,\text{kJ mol}^{-1}) - (8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (253\,\text{K})$$
$$= \boxed{83.8\,\text{kJ mol}^{-1}}$$

We assume that the reaction is first-order for which, by analogy to Section 24.4

$$K^{\ddagger} = K = \frac{kT}{h\nu}\overline{K}^{\ddagger}$$

and $k_1 = k^{\ddagger}K^{\ddagger} = \nu \times \dfrac{kT}{h\nu} \times \overline{K}^{\ddagger}$

with $\Delta^{\ddagger}G = -RT\,\ln \overline{K}^{\ddagger}$

Therefore, $k_1 = A\,e^{-E_a/RT} = \frac{kT}{h}\,e^{-\Delta^{\ddagger}G/RT} = \frac{kT}{h}\,e^{\Delta^{\ddagger}S/R}\,e^{-\Delta^{\ddagger}H/RT}$

and hence we can identify $\Delta^{\ddagger}S$ by writing

$$k_1 = \frac{kT}{h}\,e^{\Delta^{\ddagger}S/R}\,e^{-E_a/RT}\,e = A\,e^{-E_a/RT}$$

and hence obtain

$$\Delta^{\ddagger}S = R\left[\ln\left(\frac{hA}{kT}\right) - 1\right]$$
$$= 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times \left[\ln\left(\frac{(6.626\times10^{-34}\,\text{J s}) \times (1.4\times10^{14}\,\text{s}^{-1})}{(1.381\times10^{-23}\,\text{J K}^{-1}) \times (253\,\text{K})}\right) - 1\right]$$
$$= \boxed{+19.1\,\text{J K}^{-1}\,\text{mol}^{-1}}$$

Therefore, $\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 83.8\,\text{kJ mol}^{-1} - 253\,\text{K} \times 19.1\,\text{J K}^{-1}\text{mol}^{-1}$

$$= \boxed{+79.0\,\text{kJ mol}^{-1}}$$

P24.6 Figure 24.3 shows that $\log k$ is proportional to the ionic strength for neutral molecules.

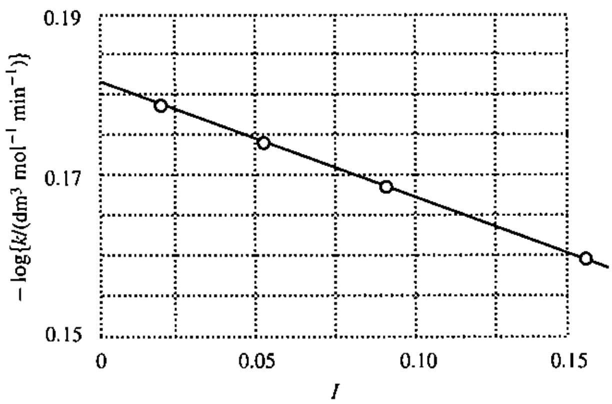


Figure 24.3

From the graph, the intercept at $I = 0$ is -0.182, so

$$k^\circ = \boxed{0.658\,\mathrm{dm^3\,mol^{-1}\,min^{-1}}}$$

COMMENT. In comparison to the effect of ionic strength on reactions in which two or more reactants are ions, the effect when only one is an ion is slight, in rough qualitative agreement with eqn 24.69.

P24.8 Both approaches involve plots of $\log k$ versus $\log \gamma$, where γ is the activity coefficient. The limiting law has $\log \gamma$ proportional to $I^{1/2}$ (where I is ionic strength), so a plot of $\log k$ versus $I^{1/2}$ should give a straight line whose y-intercept is $\log k^\circ$ and whose slope is $2Az_Az_B$, where z_A and z_B are charges involved in the activated complex. The extended Debye–Hückel law has $\log \gamma$ proportional to $[I^{1/2}/(1 + BI^{1/2})]$, so it requires plotting $\log k$ versus $[I^{1/2}/(1 + BI^{1/2})]$, and it also has a slope of $2Az_Az_B$ and a y-intercept of $\log k^\circ$. The ionic strength in a 2 : 1 electrolyte solution is three times the molar concentration. The transformed data and plot (Figure 24.4) follow

$[Na_2SO_4]/(\mathrm{mol\,kg^{-1}})$	0.2	0.15	0.1	0.05	0.025	0.0125	0.005
$k/(\mathrm{dm^{3/2}\,mol^{-1}s^{-1}})$	0.462	0.430	0.390	0.321	0.283	0.252	0.224
$I^{1/2}$	0.775	0.671	0.548	0.387	0.274	0.194	0.122
$I^{1/2}(1 + BI^{1/2})$	0.436	0.401	0.354	0.279	0.215	0.162	0.109
$\log k$	−0.335	−0.367	−0.409	−0.493	−0.548	−0.599	−0.650

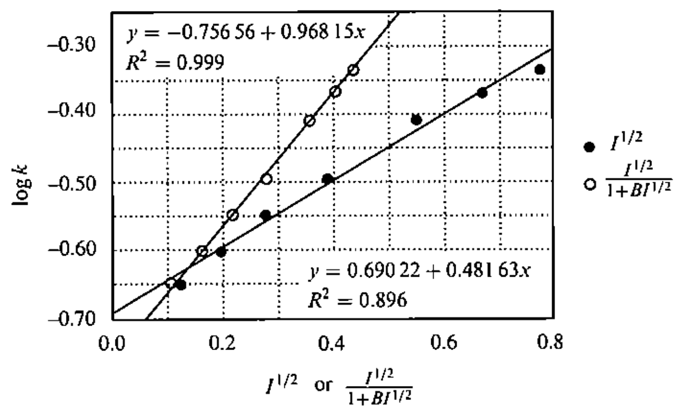


Figure 24.4

The line based on the limiting law appears curved. The zero-ionic-strength rate constant based on it is

$$k^\circ = 10^{-0.690}\,\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}} = 0.204\,\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}}$$

The slope is positive, so the complex must overcome repulsive interactions. The product of charges, however, works out to be 0.5, not easily interpretable in terms of charge numbers. The line based on the extended law appears straighter and has a better correlation coefficient. The zero-ionic-strength rate constant based on it is

$$k^\circ = 10^{-0.757}\,\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}} = 0.175\,\mathrm{dm^{3/2}\,mol^{-1/2}\,s^{-1}}$$

The product of charges works out to be 0.9, nearly 1, interpretable in terms of $\boxed{\text{a complex of two univalent ions of the same sign}}$

P24.10 $\mathrm{A + A \rightarrow A_2} \quad \Delta\nu = -1$

$$\Delta^{\ddagger}S = R\left(\ln\left[\frac{A}{(kT/h)\times(RT/p^{\ominus})}\right]+2\right) \quad [24.63]$$

$$= -(8.3145\,\mathrm{J\,K^{-1}mol^{-1}})$$

$$\times\left[\ln\left[\frac{4.07\times10^{5}\,\mathrm{M^{-1}\,s^{-1}}\,(m^3/10^3\,\mathrm{dm^3})}{\frac{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(300\,\mathrm{K})^2\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(1.013\times10^{5}\,\mathrm{Pa})}}\right]+2\right]$$

$$= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times[\ln(2.631\times10^{-9})+2]$$

$$\boxed{\Delta^{\ddagger}S = -148\,\mathrm{J\,K^{-1}\,mol^{-1}}}$$

$$\Delta^{\ddagger}H = E_a - 2RT = 65.43\,\mathrm{kJ\,mol^{-1}} - 2\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(300\,\mathrm{K})$$

$$\times\left(\frac{10^{-3}\,\mathrm{kJ}}{\mathrm{J}}\right) \quad [24.60, 24.61]$$

$$\boxed{\Delta^{\ddagger}H = 60.44\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta^{\ddagger}H = \Delta^{\ddagger}U + \Delta^{\ddagger}(pV)$$

$$\Delta^{\ddagger}U = \Delta^{\ddagger}H - \Delta^{\ddagger}(pV) = \Delta^{\ddagger}H - \Delta\nu RT$$

$$= (60.44\,\mathrm{kJ\,mol^{-1}}) - (-1)\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(300\,\mathrm{K})\times\left(\frac{10^{-3}\,\mathrm{kJ}}{\mathrm{J}}\right)$$

$$\boxed{\Delta^{\ddagger}U = 62.9\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S = 60.44\,\mathrm{kJ\,mol^{-1}} - (300\,\mathrm{K})\times(-148\,\mathrm{J\,K^{-1}\,mol^{-1}})$$

$$\times\left(\frac{10^{-3}\,\mathrm{kJ}}{\mathrm{J}}\right) \quad [24.59]$$

$$\boxed{\Delta^{\ddagger}G = 104.8\,\mathrm{kJ\,mol^{-1}}}$$

P24.12 Estimate the bimolecular rate constant k_{12} for the reaction

$$\mathrm{Ru(bpy)_3{}^{3+} + Fe(H_2O)_6{}^{2+} \rightarrow Ru(bpy)_3{}^{2+} + Fe(H_2O)_6{}^{3+}}$$

by using the approximate Macrus cross-relation:

$$k_{12} \approx (k_{11}k_{22}K)^{1/2}.$$

The standard cell potential for the reaction is:

$$E^{\ominus} = E^{\ominus}_{\text{red}}(\text{Ru(bpy)}_3{}^{3+}) - E^{\ominus}_{\text{red}}(\text{Fe(H}_2\text{O)}_6{}^{3+}) = (1.26 - 0.77)\,\text{V} = 0.49\,\text{V}$$

The equilibrium constant is:

$$K = \exp\left(\frac{\nu F E^{\ominus}}{RT}\right) = \exp\left(\frac{(1)(96485\,\text{C mol}^{-1}\,\text{s}^{-1})(0.49\,\text{V})}{(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1})(298\,\text{K})}\right) = 1.9 \times 10^{8}$$

The rate constant is approximately:

$$k_{12} \approx [(4.0 \times 10^{8}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1})(4.2\,\text{dm}^3\,\text{mol}^{-1}\text{s}^{-1})(1.9 \times 10^{8})]^{1/2},$$

$$k_{12} \approx \boxed{5.6 \times 10^{8}\,\text{dm}^3\,\text{mol}^{-1}\text{s}^{-1}}$$

Solutions to theoretical problems

P24.14 Programs for numerical integration using, for example, Simpson's rule are readily available for personal computers and hand-held calculators. Simplify the form of eqn 24.40 by writing

$$z^2 = \frac{kx^2}{4D}, \quad \tau = kt, \quad j = \left(\frac{A}{n_0}\right)\left(\frac{\pi D}{k}\right)^{1/2} [\text{J}]^*$$

Then evaluate

$$j = \int_0^{\tau} \left(\frac{1}{\tau}\right)^{1/2} e^{-z^2/\tau} e^{-\tau}\,d\tau + \left(\frac{1}{\tau}\right)^{1/2} e^{-z^2/\tau} e^{-\tau}$$

for various values of k.

P24.16
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]\gamma_{\text{HA}}}\gamma_{\pm}{}^2 \approx \frac{[\text{H}^+][\text{A}^-]\gamma_{\pm}^2}{[\text{HA}]}$$

Therefore, $[\text{H}^+] = \dfrac{[\text{HA}]K_a}{[\text{A}^-]\gamma_{\pm}^2}$

and $\log[\text{H}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]} - 2\log\gamma_{\pm} = \log K_a + \log\frac{[\text{HA}]}{[\text{A}^-]} + 2AI^{1/2}$

Write $v = k_2[\text{H}^+][\text{B}]$

then

$$\begin{aligned}
\log v &= \log(k_2[\text{B}] + \log[\text{H}^+] \\
&= \log(k_2[\text{B}]) + \log\frac{[\text{HA}]}{[\text{A}^-]} + 2AI^{1/2} + \log K_a \\
&= \log v^{\circ} + 2AI^{1/2}, \quad v^{\circ} = k_2\frac{[\text{B}][\text{HA}]K_a}{[\text{A}^-]}
\end{aligned}$$

That is, the logarithm of the rate should depend linearly on the square root of the ionic strength, $\boxed{\log v \propto I^{1/2}}$

P24.18

$$k_1 = \frac{kT}{h} \times \frac{q^{\ddagger}}{q} e^{-\beta \Delta E} \text{ [Problem 24.17]}$$

$$q^{\ddagger} = q_z^{\ddagger V} q_y^{\ddagger V} q_x^{R} \approx \left(\frac{kT}{h\nu^{\ddagger}}\right)^2 q^{R}$$

$$q^{R} \approx \frac{1.027}{\sigma} \times \frac{(T/\mathrm{K})^{3/2}}{(B/\mathrm{cm}^{-1})^{3/2}} \text{ [Table 20.4, } A = B = C] \approx 80$$

$$q = q_z^{V} q_y^{V} q_x^{V} \approx \left(\frac{kT}{h\nu}\right)^3$$

Therefore, $k_1 \approx 80 \times \frac{\nu^3}{\nu^{\ddagger 2}} e^{-\beta \Delta E_0} \approx 80 \times 5.4 \times 10^4\,\mathrm{s}^{-1}$ [Problem 24.15] $= 4 \times 10^6\,\mathrm{s}^{-1}$

Consequently, $D \approx (80) \times (2.7 \times 10^{-15}\,\mathrm{m}^2\,\mathrm{s}^{-1}) = \boxed{2 \times 10^{-13}\,\mathrm{m}^2\,\mathrm{s}^{-1}}$ if $\nu^{\ddagger} = \nu$ and $\boxed{9 \times 10^{-13}\,\mathrm{m}^2\,\mathrm{s}^{-1}}$ if $\nu^{\ddagger} = \frac{1}{2}\nu$.

P24.20 It follows that, since $\mathcal{N}_s$ and l are the same for the two experiments,

$$\frac{\sigma(\mathrm{CH_2F_2})}{\sigma(\mathrm{Ar})} = \frac{\ln 0.6}{\ln 0.9} \text{ [Problem 24.17]} = \boxed{5}$$

CH_2F_2 is a polar molecule; Ar is not. CsCl is a polar ion pair and is scattered more strongly by the polar CH_2F_2.

P24.22 We use the Eyring equation (combining eqns 24.53 and 24.51) to compute the bimolecular rate constant

$$k_2 = \kappa \frac{kT}{h}\left(\frac{RT}{p^{\ominus}}\right) \frac{N_A \bar{q}_{C^{\ddagger}}^{\ominus}}{q_H^{\ominus} q_{D_2}^{\ominus}} \exp\left(\frac{-\Delta E_0}{RT}\right) \approx \frac{(RT)^2 \bar{q}_{C^{\ddagger}}^{\ominus}}{hp^{\ominus} q_H^{\ominus} q_{D_2}^{\ominus}} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

We are to consider a variety of activated complexes, but the reactants, (H and D_2) and their partition functions do not change. Consider them first. The partition function of H is solely translational:

$$q_H^{\ominus} = \frac{RT}{p^{\ominus} \Lambda_{D_2}^3} \quad \text{and} \quad \Lambda_H = \left(\frac{h^2}{2\pi\kappa T m_H}\right)^{1/2} \quad \text{so} \quad q_H^{\ominus} = \frac{RT(2\pi\kappa T m_H)^{3/2}}{p^{\ominus} h^3}$$

We have neglected the spin degeneracy of H, which will cancel with the spin degeneracy of the activated complex. The partition function of D_2 has a rotational term as well.

$$q_{D_2}^{\ominus} = \frac{RT}{p^{\ominus} \Lambda_{D_2}^3} \times \frac{kT}{\sigma hcB_{D_2}} = \frac{RkT^2(2\pi kTm_{D_2})^{3/2}}{2p^{\ominus} h^4 cB_{D_2}}$$

We have neglected the vibrational partition function of D_2, which is very close to unity at the temperature in question. The symmetry number σ is 2 for a homonuclear diatomic, and the rotational constant is $30.44\,\mathrm{cm}^{-1}$. Now, the partition function of the activated complex will have a translational piece that is the same regardless of the model:

$$\bar{q}_{C^{\ddagger}}^{\ominus} = q_{C^{\ddagger},\mathrm{trans}}^{\ominus} \times q_{C^{\ddagger},\mathrm{rot}} \times \bar{q}_{C^{\ddagger},\mathrm{vib}}$$

$$\text{where } q_{C^{\ddagger},\mathrm{trans}}^{\ominus} = \frac{RT(2\pi\kappa T m_{HD_2})^{3/2}}{p^{\ominus} h^3}$$

Let us aggregate the model-independent factors into a single term, F where:

$$F = \frac{(RT)^2 q^{\ominus}_{\text{C}^\ddagger,\text{trans}}}{hp^{\ominus} q^{\ominus}_{\text{H}} q^{\ominus}_{\text{D}_2}} \exp\left(\frac{-\Delta E_0}{RT}\right) = \frac{2h^3 c B_{\text{D}_2} m_{\text{HD}_2}{}^{3/2}}{kT(2\pi m_{\text{H}} m_{\text{D}_2} kT)^{3/2}} \exp\left(\frac{-\Delta E_0}{RT}\right)$$

$$F = h^3 c B_{\text{D}_2}\left(\frac{5^3}{2m_{\text{H}}^3 (4)^3 \pi^3 T^3 k^5}\right)^{1/2} \exp\left(\frac{-\Delta E_0}{RT}\right) = 2.71 \times 10^4\,\text{dm}^3\,\text{mol}^{-1} s^{-1}$$

where we have taken $m_{HD_2} = 5m_H$ and $m_{D_2} = 4m_H$.

Now $\kappa_2 = F \times q_{\text{C}^\ddagger,\text{rot}} \times \overline{q}_{\text{C}^\ddagger,\text{vib}}$. The number of vibrational modes in the activated complex is $3 \times 3 - 6 = 3$ for a nonlinear complex, one more for a linear complex; however, in either case, one mode is the reaction coordinate, and is removed from the partition function. Therefore, assuming all real vibrations to have the same wavenumber $\tilde{\nu}$

$$\overline{q}_{\text{C}^\ddagger} = q^2_{\text{mode}}(\text{nonlinear}) \text{ or } q^3_{\text{mode}}(\text{linear})$$

where

$$q_{\text{mode}} = \left[1 - \exp\left(\frac{-hc\tilde{\nu}}{kT}\right)\right]^{-1} = 1.028$$

if the vibrational wavenumbers are $1000\,\text{cm}^{-1}$. The rotational partition function is

$$q_{\text{C}^\ddagger,\text{rot}} = \frac{kT}{\sigma hcB}(\text{linear}) \text{ or } \frac{1}{\sigma}\left(\frac{\kappa T}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} (\text{nonlinear})$$

where the rotational constants are related to moments of inertia by

$$B = \frac{\hbar}{4\pi cI} \text{ where } I = \sum mr^2$$

and r is the distance from an atom to a rotational axis.

(a) The first model for the activated complex is triangular, with two equal sides of

$$s = 1.30(74\text{ pm}) = 96\text{ pm}$$

and a base of

$$b = 1.20(74\,\text{pm}) = 89\,\text{pm}$$

The moment of inertia about the axis of the altitude of the triangle (z-axis) is

$$I_1 = 2m_{\text{D}}(b/2)^2 = m_{\text{H}}b^2 \text{ so } A = \frac{\hbar}{4\pi c m_{\text{H}} b^2} = 21.2\,\text{cm}^{-1}$$

To find the other moments of inertia, we need to find the center of mass. Clearly it is in the plane of the molecule and on the z-axis; the center of mass is the position z at which

$$\sum_i m_i(z_i - z) = 0 = 2(2m_{\text{H}})(0 - z) + m_{\text{H}}(H - z)$$

where H is the height of the triangle,

$$H = [s^2 - (b/2)^2]^{1/2} = 85\,\text{pm}$$

so the center of mass is

$$z = H/5$$

The moment of inertia about the axis in the plane of the triangle perpendicular to the altitude is

$$I_2 = 2(2m_H)(H/5)^2 + m_H(4H/5)^2 = (4m_H/5)H^2$$

so $B = \dfrac{\hbar}{4\pi c(4m_H/5)H^2} = 28.3\,\text{cm}^{-1}$

The distance from the center of mass to the D atoms is

$$r_D = [(H/5)^2 + (b/2)^2]^{1/2} = 48\,\text{pm}$$

and the moment of inertia about the axis perpendicular to the plane of the triangle is

$$I_3 = 2(2m_H)r_D^2 + m_H(4H/5)^2 = 2(2m_H)[(H/5)^2 + (b/2)^2] + m_H(4H/5)^2$$

$$I_3 = (4m_H/5)(s^2 + b^2)$$

so $C = \dfrac{\hbar}{4\pi c(4m_H/5)(s^2 + b^2)} = 12.2\,\text{cm}^{-1}$. The rotational partition function is:

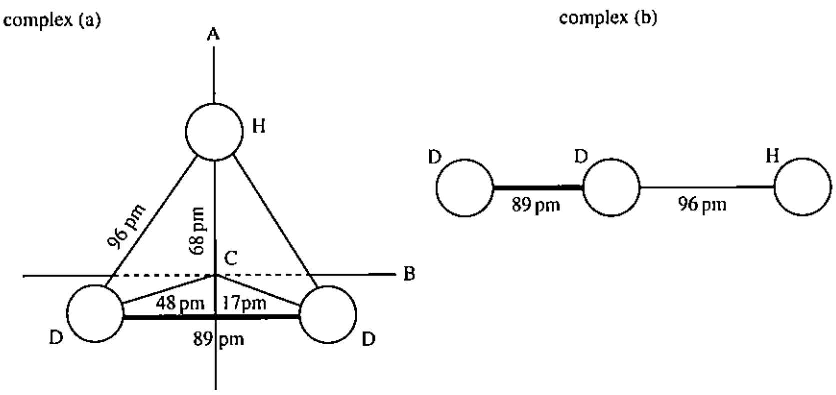
$$q_{C^\ddagger,\text{rot}} = \frac{1}{s}\left(\frac{kT}{hc}\right)^{3/2}\left(\frac{\pi}{ABC}\right)^{1/2} = 47.7$$

(The symmetry number σ is 2 for this model.) The vibrational partition function is

$$\overline{q}_{C^\ddagger,\text{vib}} = q_{\text{mode}}^2 = 1.057$$

So the rate constant is:

$$k_2 = F \times q_{C^\ddagger,\text{rot}} \times \overline{q}_{C^\ddagger,\text{vib}} = \boxed{1.37 \times 10^6\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$



(b) To compute the moment of inertia, we need the center of mass. Let the terminal D atom be at $x = 0$, the central D atom at $x = b$, and the H atom at $x = b + s$. The center of mass is the position X at which

$$\sum_i m_i(x_i - X) = 0 = 2m_H(0 - X) + 2m_H(b - X) + m_H(s + b - X)$$

$$5X = 3b + s \text{ so } x = (3b + s)/5$$

The moment of inertia is

$$I = \sum_i m_i(x_i - X)^2 = 2m_H X^2 + 2m_H(b - X)^2 + m_H(s + b - X)^2$$

$$= 3.97 \times 10^{-47}\,\mathrm{m\,kg^2}$$

and $B = \dfrac{\hbar}{4\pi c I} = 7.06\,\mathrm{cm^{-1}}$. The rotational partition function is

$$q_{C^\ddagger,\mathrm{rot}} = \frac{kT}{\sigma hcB} = 39.4$$

(The symmetry number σ is 1 for this model.) The vibrational partition function is

$$\bar{q}_{C^\ddagger,\mathrm{vib}} = q^3_{\mathrm{mode}} = 1.09$$

So the rate constant is

$$k_2 = F \times q_{C^\ddagger,\mathrm{rot}} \times \bar{q}_{C^\ddagger,\mathrm{vib}} = \boxed{1.16 \times 10^6\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

(c) Both models are already pretty good, coming within a factor of 3 to 4 of the experimental result, and neither model has much room for improvement. Consider how to try to change either model to reduce the rate constant toward the experimental value. The factor F is model-independent. The factor $\bar{q}_{C^\ddagger,\mathrm{vib}}$ is nearly at its minimum possible value, 1, so stiffening the vibrational modes will have almost no effect. Only the factor $q_{C^\ddagger,\mathrm{rot}}$ is amenable to lowering, and even that not by much. It would be decreased if the rotational constants were increased, which means decreasing the moments of inertia and the bond lengths. Reducing the lengths s and b in the models to the equilibrium bond length of H_2 would only drop k_2 to 6.5×10^5 (model a) or 6.9×10^5 (model b) $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, even with a stiffening of vibrations. Reducing the HD distance in model a to 80% of the H_2 bond length does produce a rate constant of $4.2 \times 10^5\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ (assuming stiff vibrations of $2000\,\mathrm{cm^{-1}}$); such a model is not intermediate in structure between reactants and products, though. It appears that the rate constant is rather insensitive to the geometry of the complex.

Solutions to applications

P24.24 **(a)** The rate constant of a diffusion-limited reaction is

$$k = \frac{8RT}{3\eta} = \frac{8 \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times (298\,\mathrm{K}) \times (10^3\,\mathrm{dm^3\,m^{-3}})}{3 \times (1.06 \times 10^{-3}\,\mathrm{kg\,m^{-1}s^{-1}})}$$

$$= \boxed{6.23 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}}$$

(b) The rate constant is related to the diffusion constants and reaction distance by

$$k = 4\pi R^* D N_A \quad \text{so} \quad R^* = \frac{k}{4\pi D N_A}$$

$$= \frac{(2.77 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}) \times (10^{-3}\ \mathrm{m^{-3}\ dm^{-3}})}{4\pi \times (1 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}) \times (6.022 \times 10^{23}\ \mathrm{mol^{-1}})}$$

$$R^* = \boxed{3.7 \times 10^{-10}\ \mathrm{m\ or}\ 0.37\ \mathrm{nm}}$$

P24.26 For a series of reactions with a fixed edge-to-edge distance and reorganization energy, the log of the rate constant depends quadratically on the reaction free-energy; eqn 24.84 applies: $\ln k_{\mathrm{et}} = -((\Delta_r G^{\ominus})^2/4\lambda kT) - (\Delta_r G^{\ominus}/2kT) + \text{constant}$,

where we have replaced RT by kT since the energies are given in molecular rather than molar units.

Draw up the following table:

$\Delta_r G^{\ominus}/\mathrm{eV}$	$K_{\mathrm{et}}/(10^6\ \mathrm{s^{-1}})$	$\ln K_{\mathrm{et}}/\mathrm{s^{-1}}$
−0.665	0.657	13.4
−0.705	1.52	14.2
−0.745	1.12	13.9
−0.975	8.99	16.0
−1.015	5.76	15.6
−1.055	10.1	16.1

and plot $\ln k_{\mathrm{et}}$ vs. $\Delta_r G^{\ominus}$ (see Figure 24.5)

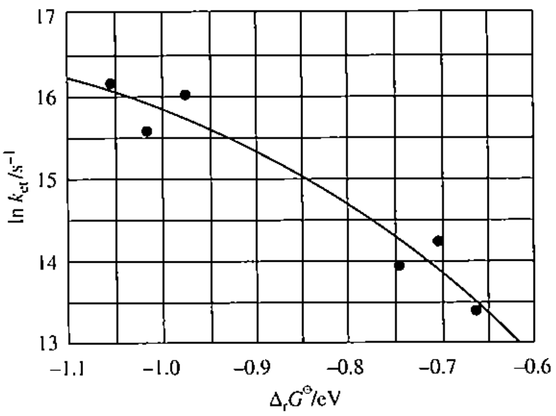


Figure 24.5

The least squares quadratic fit equation is:

$$\ln k_{\mathrm{et}}/\mathrm{s^{-1}} = 3.23 - 21.1(\Delta_r G^{\ominus}/\mathrm{eV}) - 8.48 - (\Delta_r G^{\ominus}/\mathrm{eV})^{-2}\ r^2 = 0.938$$

The coefficient of the quadratic term is:

$$-\frac{1}{4\lambda kt} = -\frac{8.48}{\text{eV}^2},$$

so $$\lambda = \frac{(\text{eV})^2}{4(8.48)\,kT} = \frac{(1.602 \times 10^{-19}\,\text{J}\,\text{eV}^{-1})(\text{eV})^2}{2(8.48)(1.381 \times 10^{-23}\,\text{J}\,\text{K}^{-1})(298\,\text{K})},$$

$$\boxed{\lambda = 2.30\,\text{eV}}$$

As a check on the reliablilty of the fit, note that according to eqn 24.84, the coefficient of the linear term is:

$$\frac{1}{2kT} = -\frac{21.1}{\text{eV}},$$

so $$T = \frac{\text{eV}}{2k(21.1)} = \frac{(1.602 \times 10^{-19}\,\text{J}\,\text{eV}^{-1})\text{eV}}{2(1.381 \times 10^{-23}\,\text{J}\,\text{K}^{-1})(21.1)} = \boxed{275\,\text{K}},$$

which differs by about 8% from the stated temperature of 298 K.

P24.28 The theoretical treatment of section 24.11 applies only at relatively high temperatures. At temperatures above 130 K, the reaction in question is observed to follow a temperature dependence consistent with eqn 24.81, namely increasing rate with increasing temperature. Below 130 K, the temperature dependent terms in eqn 24.81 are replaced by Frank–Condon factors; that is, temperature-dependent terms are replaced by temperature-independent wavefunction overlap integrals.

25 Processes at solid surfaces

Answers to discussion questions

D25.2 (a) AES can provide a depth profile or fingerprint of the sample, since the Auger spectrum is characteristic of the material present. Information about the atoms present and their bonding can be obtained. The technique is limited to a depth of about 100 nm.

EELS and HREELS can detect very tiny amounts of adsorbate. The incident beam can induce vibrational excitations in the absorbate that is characteristic of the species and its environment.

RAIRS resolves the problem of the opacity of surfaces to infrared or visible radiation but the spectral bands observed are typically very weak.

SERS resolves the problem of weak spectral observed in RAIRS. It generally gives a greatly enhanced resonance Raman intensity. The disadvantages are that it provides only a weak enhancement for flat single crystal surfaces and the technique works well only for certain metals.

SEXAFS can provide nearest neighbor distributions, giving the number and interatomic distances of surface atoms

SHG provides information about adsorption and surface coverage and rapid surface changes.

UPS can provide detailed information about the chemisorption process, surface composition, and the oxidation state of atoms. It can distinguish between chemical absorption and physical adsorption.

XPS is similar to UPS in the information revealed.

See the references listed under *Further reading* for more information about these modern techniques for probing the properties of surfaces.

(b) Consult the appropriate sections of the textbook (listed below) for the advantages and limitations of each technique.

AFM: 28.2(h) and Box 28.1; FIM: 25.5(b); LEED: 25.2(e); MBRS: 25.7(c); MBS: 25.2(f); SAM: 25.2(c); SEM: 28.2(h); and STM: 25.5(b).

D25.4
$$R_{eq} = R_{max}\left(\frac{a_0K}{a_0K+1}\right)$$

Taking the inverse of the above equation and multiplication by a_0 gives:

$$\frac{a_0}{R_{eq}} = \frac{1}{R_{max}K} + \frac{a_0}{R_{max}}$$

This working equation predicts that a plot of a_0/R_{eq} against a_0 should be linear if the model is applicable to the experimental data. The slope of a linear regression fit to the data gives the value of $1/R_{max}$ or $R_{max} = 1/\text{slope}$. Likewise, the regression intercept equals $1/R_{max}K$ or $K = \text{slope/intercept}$.

D25.6 Heterogeneous catalysis on a solid surface requires the reacting molecules or fragments to encounter each other by adsorption on the surface. Therefore, the rate of the catalysed reaction is determined by the sticking probabilities of the species on the surface as described by Figure 25.28 of the text.

D25.8 (a) There are three models of the structure of the electrical double layer. The Helmholtz model, the Gouy–Chapman model, and the Stern model. We will describe the Stern model which is a combination of the first two and illustrates most of the structural features associated with the double layer. The electrode surface is a rigid plane of, say, excess positive charge. Next to it is a plane of negatively charged ions with their solvating molecules, called the outer Helmholtz layer. Adjoining this region is a diffuse layer with perhaps only a slight excess of negative charge. This region fades away into the bulk neutral solution. At another level of sophistication, an inner Helmholtz plane is added, see Section 25.8(a) for a brief description of this layer.

(b) The electrical double layer is present near the electrode surface whether or not current is flowing in the cell. The Nernst diffusion layer is invoked to explain polarization effects near a working electrode and is a region of linear variation in concentration between the bulk solution and outer Helmholtz plane. It is typically 0.1–0.5 mm in thickness without stirring or convection, but can be reduced to 0.001 mm with such agitation The electrical double layer is unaffected by hydrodynamic flow and is typically about 1 nm in thickness.

D25.10 In cyclic voltammetry, the current at a working electrode is monitored as the applied potential difference is changed back and forth at a constant rate between pre-set limits (Figs 25.45 and 25.46). As the potential difference approaches $E^\ominus$ (Ox, Red) for a solution that contains the reduced component (Red), current begins to flow as Red is oxidized. When the potential difference is swept beyond $E^\ominus$ (Ox, Red), the current passes through a maximum and then falls as all the Red near the electrode is consumed and converted to Ox, the oxidized form. When the direction of the sweep is reversed and the potential difference passes through $E^\ominus$ (Ox, Red), current flows in the reverse direction. This current is caused by the reduction of the Ox formed near the electrode on the forward sweep. It passes through the maximum as Ox near the electrode is consumed. The forward and reverse current maxima bracket $E^\ominus$ (Ox, Red), so the species present can be identified. Furthermore, the forward and reverse peak currents are proportional to the concentration of the couple in the solution, and vary with the sweep rate. If the electron transfer at the electrode is rapid, so that the ratio of the concentrations of Ox and Red at the electrode surface have their equilibrium values for the applied potential (that is, their relative concentrations are given by the Nernst equation), the voltammetry is said to be *reversible*. In this case, the peak separation is independent of the sweep rate and equal to $(59\,\mathrm{mV})/n$ at room temperature, where n is the number of electrons transferred. If the rate of electron transfer is low, the voltammetry is said to be *irreversible*. Now, the peak separation is greater than $(59\,\mathrm{mV})/n$ and increases with increasing sweep rate. If homogeneous chemical reactions accompany the oxidation or reduction of the couple at the electrode, the shape of the voltammogram changes, and the observed changes give valuable information about the kinetics of the reactions as well as the identities of the species present.

D25.12 Corrosion is an electrochemical process. We will illustrate it with the example of the rusting of iron, but the same principles apply to other corrosive processes. The electrochemical basis of corrosion that occurs in the presence of water and oxygen, is revealed by comparing the standard potentials of the metal reduction, such as

$$\mathrm{Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)} \qquad E^\ominus = -0.44\,\mathrm{V}$$

with the values for one of the following half-reactions

In acidic solution

(a) $2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad E^\ominus = 0\,V$

(b) $4H^+(aq) + O_2(g) + 4e^- \rightarrow 2H_2O(l) \qquad E^\ominus = +1.23\,V$

In basic solution:

(c) $2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-(aq) \qquad E^\ominus = +0.40\,V$

Because all three redox couples have standard potentials more positive than $E^\ominus(Fe^{2+}/Fe)$, all three can drive the oxidation of iron to iron(II). The electrode potentials we have quoted are standard values, and they change with the pH of the medium. For the first two

$$E(a) = E^\ominus(a) + (RT/F)\ln a(H^+) = -(0.059\,V)\,pH$$
$$E(b) = E^\ominus(b) + (RT/F)\ln a(H^+) = 1.23\,V - (0.059\,V)\,pH$$

These expressions let us judge at what pH the iron will have a tendency to oxidize (see Chapter 7). A thermodynamic discussion of corrosion, however, only indicates whether a tendency to corrode exists. If there is a thermodynamic tendency, we must examine the kinetics of the processes involved to see whether the process occurs at a significant rate. The effect of the exchange current density on the corrosion rate can be seen by considering the specific case of iron in contact with acidified water. Thermodynamically, either the hydrogen or oxygen reduction reaction (a) or (b) is effective. However, the exchange current density of reaction (b) on iron is only about $10^{-14}\,A\,cm^{-2}$, whereas for (a) it is $10^{-6}\,A\,cm^{-2}$. The latter therefore dominates kinetically, and iron corrodes by hydrogen evolution in acidic solution. For corrosion reactions with similar exchange current densities, eqn 25.66 predicts that the rate of corrosion is high when E is large. That is, rapid corrosion can be expected when the oxidizing and reducing couples have widely differing electrode potentials.

Several techniques for inhibiting corrosion are available. First, from eqn 25.66 we see that the rate of corrosion depends on the surfaces exposed: if either A or A' is zero, then the corrosion current is zero. This interpretation points to a trivial, yet often effective, method of slowing corrosion: cover the surface with some impermeable layer, such as paint, which prevents access of damp air. Paint also increases the effective solution resistance between the cathode and anode patches on the surface.

Another form of surface coating is provided by galvanizing, the coating of an iron object with zinc. Because the latter's standard potential is $-0.76\,V$, which is more negative than that of the iron couple, the corrosion of zinc is thermodynamically favored and the iron survives (the zinc survives because it is protected by a hydrated oxide layer).

Another method of protection is to change the electric potential of the object by pumping in electrons that can be used to satisfy the demands of the oxygen reduction without involving the oxidation of the metal. In cathodic protection, the object is connected to a metal with a more negative standard potential (such as magnesium, $-2.36\,V$). The magnesium acts as a sacrificial anode, supplying its own electrons to the iron and becoming oxidized to Mg^{2+} in the process.

Solutions to exercises

E25.1(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

(a) For N_2

(i) $$Z_W = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (10.0\,\text{Pa})}{(2\pi \times (28.013 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}))^{1/2}}$$

$$= 2.88 \times 10^{23}\,\text{m}^{-2}\,\text{s}^{-1}$$

$$= \boxed{2.88 \times 10^{19}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

(ii) $$Z_W = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (0.150 \times 10^{-6}\,\text{Torr}) \times (1.01 \times 10^{5}\,\text{Pa}/760\,\text{Torr})}{(2\pi \times (28.013 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}))^{1/2}}$$

$$= 5.75 \times 10^{17}\,\text{m}^{-2}\,\text{s}^{-1}$$

$$= \boxed{5.75 \times 10^{13}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

(b) For methane

(i) $$Z_W = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (10.0\,\text{Pa})}{(2\pi \times (16.04 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}))^{1/2}}$$

$$= 3.81 \times 10^{23}\,\text{m}^{-2}\,\text{s}^{-1}$$

$$= \boxed{3.81 \times 10^{19}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

(ii) $$Z_W = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (0.150 \times 10^{-6}\,\text{Torr}) \times (1.01 \times 10^{5}\,\text{Pa}/760\,\text{Torr})}{(2\pi \times (16.04 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}))^{1/2}}$$

$$= 7.60 \times 10^{17}\,\text{m}^{-2}\,\text{s}^{-1}$$

$$= \boxed{7.60 \times 10^{13}\,\text{cm}^{-2}\,\text{s}^{-1}}$$

E25.2(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}} \quad \text{so} \quad p = \frac{Z_W A (2\pi MRT)^{1/2}}{N_A A}$$

$$p = \frac{(5.00 \times 10^{19}\,\text{s}^{-1})}{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times \pi \times (1/2 \times 2.0 \times 10^{-3}\,\text{m})^2}$$
$$\times (2\pi \times (28.013 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (525\,\text{K}))^{1/2}$$

$$= \boxed{7.3 \times 10^{2}\,\text{Pa}}$$

E25.3(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi M RT)^{1/2}}$$

so the rate of collision per Fe atom will be $Z_W A$ where A is the area per Fe atom. The exposed surface consists of faces of the bcc unit cell, with one atom per face. So the area per Fe is

$$A = c^2 \quad \text{and} \quad \text{rate} = Z_W A = \frac{N_A p c^2}{(2\pi M RT)^{1/2}}$$

where c is the length of the unit cell. So

$$\text{rate} = \frac{(6.022 \times 10^{23}\,\text{mol}^{-1}) \times (24\,\text{Pa}) \times (145 \times 10^{-12}\,\text{m})^2}{(2\pi \times (4.003 \times 10^{-3}\,\text{kg mol}^{-1}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (100\,\text{K}))^{1/2}}$$

$$= \boxed{6.6 \times 10^4\,\text{s}^{-1}}$$

E25.4(b) The number of CO molecules adsorbed on the catalyst is

$$N = nN_A = \frac{pVN_A}{RT} = \frac{(1.00\,\text{atm}) \times (4.25 \times 10^{-3}\,\text{dm}^3) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})}$$

$$= 1.14 \times 10^{20}$$

The area of the surface must be the same as that of the molecules spread into a monolayer, namely, the number of molecules times each one's effective area

$$A = Na = (1.14 \times 10^{20}) \times (0.165 \times 10^{-18}\,\text{m}^2) = \boxed{18.8\,\text{m}^2}$$

E25.5(b) If the adsorption follows the Langmuir isotherm, then

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad K = \frac{\theta}{p(1-\theta)} = \frac{V/V_{\text{mon}}}{p(1 - V/V_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for V_{mon}

$$\frac{V_1/V_{\text{mon}}}{p_1(1 - V_1/V_{\text{mon}})} = \frac{V_2/V_{\text{mon}}}{p_2(1 - V_2/V_{\text{mon}})} \quad \text{so} \quad \frac{p_1(V_{\text{mon}} - V_1)}{V_1} = \frac{p_2(V_{\text{mon}} - V_2)}{V_2}$$

$$V_{\text{mon}} = \frac{p_1 - p_2}{p_1/V_1 - p_2/V_2} = \frac{(52.4 - 104)\,\text{kPa}}{(52.4/1.60 - 104/2.73)\,\text{kPa cm}^{-3}} = \boxed{9.7\,\text{cm}^3}$$

E25.6(b) The mean lifetime of a chemisorbed molecule is comparable to its half-life:

$$t_{1/2} = \tau_0 \exp\left(\frac{E_d}{RT}\right) \approx (10^{-14}\,\text{s}) \exp\left(\frac{155 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}\right) = \boxed{200\,\text{s}}$$

E25.7(b) The desorption rate constant is related to the half-life by

$$t = (\ln 2)/k_d \quad \text{so} \quad k_d = (\ln 2)/t$$

The desorption rate constant is related to its Arrhenius parameters by

$$k_d = A \exp\left(\frac{-E_d}{RT}\right) \quad \text{so} \quad \ln k_d = \ln A - \frac{E_d}{RT}$$

$$\text{and } E_d = \frac{(\ln k_1 - \ln k_2)R}{T_2^{-1} - T_1^{-1}} = \frac{(\ln 1.35 - \ln 1) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}{(600\,\text{K})^{-1} - (1000\,\text{K})^{-1}}$$

$$E_d = \boxed{3.7 \times 10^3\,\text{J mol}^{-1}}$$

E25.8(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad p = \frac{\theta}{K(1-\theta)}$$

(a) $$p = \frac{0.20}{(0.777\ \text{kPa}^{-1}) \times (1-0.20)} = \boxed{0.32\ \text{kPa}}$$

(b) $$p = \frac{0.75}{(0.777\ \text{kPa}^{-1}) \times (1-0.75)} = \boxed{3.9\ \text{kPa}}$$

E25.9(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp}$$

We are looking for θ, so we must first find K or m_{mon}

$$K = \frac{\theta}{p(1-\theta)} = \frac{m/m_{\text{mon}}}{p(1-m/m_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for m_{mon}

$$\frac{m_1/m_{\text{mon}}}{p_1(1-m_1/m_{\text{mon}})} = \frac{m_2/m_{\text{mon}}}{p_2(1-m_2/m_{\text{mon}})} \quad \text{so} \quad \frac{p_1(m_{\text{mon}}-m_1)}{m_1} = \frac{p_2(m_{\text{mon}}-m_2)}{m_2}$$

$$m_{\text{mon}} = \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} = \frac{(36.0-4.0)\ \text{kPa}}{(36.0/0.63 - 4.0/0.21)\ \text{kPa mg}^{-1}} = 0.84\ \text{mg}$$

So $\theta_1 = 0.63/0.84 = \boxed{0.75}$ and $\theta_2 = 0.21/0.84 = \boxed{0.25}$

E25.10(b) The mean lifetime of a chemisorbed molecule is comparable to its half-life

$$t_{1/2} = \tau_0 \exp\left(\frac{E_d}{RT}\right)$$

(a) At 400 K: $$t_{1/2} = (0.12 \times 10^{-12}\ \text{s}) \exp\left(\frac{20 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (400\ \text{K})}\right)$$

$$= \boxed{4.9 \times 10^{-11}\ \text{s}}$$

At 800 K: $$t_{1/2} = (0.12 \times 10^{-12}\ \text{s}) \exp\left(\frac{20 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (800\ \text{K})}\right)$$

$$= \boxed{2.4 \times 10^{-12}\ \text{s}}$$

(b) At 400 K: $$t_{1/2} = (0.12 \times 10^{-12}\ \text{s}) \exp\left(\frac{200 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (400\ \text{K})}\right)$$

$$= \boxed{1.6 \times 10^{13}\ \text{s}}$$

At 800 K: $$t_{1/2} = (0.12 \times 10^{-12}\ \text{s}) \exp\left(\frac{200 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\text{mol}^{-1}) \times (800\ \text{K})}\right)$$

$$= \boxed{1.4\ \text{s}}$$

E25.11(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad p = \frac{\theta}{K(1-\theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1K_1 = p_2K_2 \quad \text{and} \quad p_2 = p_1\frac{K_1}{K_2}$$

$$\text{But } K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^{\ominus}}{RT}\right) \quad \text{so} \quad \frac{K_1}{K_2} = \exp\left(\frac{-\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$$

$$p_2 = p_1\exp\left(\frac{-\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$$

$$= (8.86\,\text{kPa}) \times \exp\left(\left(\frac{-12.2\times10^3\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{298\,\text{K}}-\frac{1}{318\,\text{K}}\right)\right) = \boxed{6.50\,\text{kPa}}$$

E25.12(b) The Langmuir isotherm would be

(a) $\theta = \dfrac{Kp}{1+Kp}$

(b) $\theta = \dfrac{(Kp)^{1/2}}{1+(Kp)^{1/2}}$

(c) $\theta = \dfrac{(Kp)^{1/3}}{1+(Kp)^{1/3}}$

A plot of θ versus p at low pressures (where the denominator is approximately 1) would show progressively weaker dependence on p for dissociation into two or three fragments.

E25.13(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1+Kp} \quad \text{so} \quad p = \frac{\theta}{K(1-\theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1K_1 = p_2K_2 \quad \text{and} \quad \frac{p_2}{p_1} = \frac{K_1}{K_2}$$

$$\text{But } K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^{\ominus}}{RT}\right) \quad \text{so} \quad \frac{p_2}{p_1} = \exp\left(\frac{-\Delta_{\text{ad}}H^{\ominus}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right)$$

$$\text{and } \Delta_{\text{ad}}H^{\ominus} = R\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1}\ln\frac{p_1}{p_2},$$

$$\Delta_{\text{ad}}H^{\ominus} = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times \left(\frac{1}{180\,\text{K}}-\frac{1}{240\,\text{K}}\right)^{-1} \times \left(\ln\frac{350\,\text{kPa}}{1.02\times10^3\,\text{kPa}}\right)$$

$$= -6.40\times10^4\,\text{J mol}^{-1} = \boxed{-6.40\,\text{kJ mol}^{-1}}$$

E25.14(b) The time required for a given quantity of gas to desorb is related to the activation energy for desorption by

$$t \propto \exp\left(\frac{E_d}{RT}\right) \quad \text{so} \quad \frac{t_1}{t_2} = \exp\left(\frac{E_d}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

and $E_d = R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln\frac{t_1}{t_2}$

$$E_d = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \left(\frac{1}{873\,\mathrm{K}} - \frac{1}{1012\,\mathrm{K}}\right)^{-1} \times \left(\ln\frac{1856\,\mathrm{s}}{8.44\,\mathrm{s}}\right)$$

$$= \boxed{2.85 \times 10^5\,\mathrm{J\,mol^{-1}}}$$

(a) The same desorption at 298 K would take

$$t = (1856\ \mathrm{s}) \times \exp\left(\left(\frac{2.85 \times 10^5\,\mathrm{J\,mol^{-1}}}{8.3145\ \mathrm{J\ K^{-1}mol^{-1}}}\right) \times \left(\frac{1}{298\ \mathrm{K}} - \frac{1}{873\ \mathrm{K}}\right)\right) = \boxed{1.48 \times 10^{36}\ \mathrm{s}}$$

(b) The same desorption at 1500 K would take

$$t = (8.44\,\mathrm{s}) \times \exp\left(\left(\frac{2.85 \times 10^5\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\ K^{-1}\ mol^{-1}}}\right) \times \left(\frac{1}{1500\ \mathrm{K}} - \frac{1}{1012\ \mathrm{K}}\right)\right)$$

$$= \boxed{1.38 \times 10^{-4}\,\mathrm{s}}$$

E25.15(b) Disregarding signs, the electric field is the gradient of the electrical potential

$$\mathcal{E} = \frac{\mathrm{d}\Delta\varphi}{\mathrm{d}x} \approx \frac{\Delta\phi}{d} = \frac{\sigma}{\varepsilon} = \frac{\sigma}{\varepsilon_r\varepsilon_0} = \frac{0.12\,\mathrm{C\,m^{-2}}}{(48) \times (8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}})} = \boxed{2.8 \times 10^8\,\mathrm{V\,m^{-1}}}$$

E25.16(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1-\eta_2)} \quad \text{where} \quad f = \frac{F}{RT} = \frac{1}{25.69\,\mathrm{mV}}$$

The overpotential η_2 is

$$\eta_2 = \eta_1 + \frac{1}{f(1-\alpha)}\ln\frac{j_2}{j_1} = 105\,\mathrm{mV} + \left(\frac{25.69\,\mathrm{mV}}{1-0.42}\right) \times \ln\left(\frac{72\,\mathrm{mA\,cm^{-2}}}{17.0\,\mathrm{mA\,cm^{-2}}}\right)$$

$$= \boxed{16\bar{7}\,\mathrm{mV}}$$

E25.17(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad j_0 = j e^{(\alpha-1)f\eta}$$

$$j_0 = (17.0\,\mathrm{mA\,cm^{-2}}) \times e^{[(0.42-1)\times(105\,\mathrm{mV})/(25.69\,\mathrm{mV})]} = \boxed{1.6\,\mathrm{mA\,cm^{-2}}}$$

E25.18(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1-\eta_2)} \quad \text{and} \quad j_2 = j_1 e^{(1-\alpha)f(\eta_2-\eta_1)}.$$

So the current density at 0.60 V

$$j_2 = (1.22\,\mathrm{mA\,cm^{-2}}) \times e^{\{(1-0.50)\times(0.60\,\mathrm{V}-0.50\,\mathrm{V})/(0.025\,69\,\mathrm{V})\}} = \boxed{8.5\,\mathrm{mA\,cm^{-2}}}$$

Note: the exercise says the data refer to the same material and at the same temperature as the previous Exercise (25.18(a)), yet the results for the current density at the same overpotential differ by a factor of over 5!

E25.19(b) **(a)** The Butler–Volmer equation gives

$$\begin{aligned} j &= j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}) \\ &= (2.5\times10^{-3}\,\mathrm{A\,cm^{-2}}) \times \left(e^{\{1-0.58)\times(0.30\,\mathrm{V})/(0.025\,69\,\mathrm{V})\}} - e^{-\{(0.58)\times(0.30\,\mathrm{V})/0.025\,69\,\mathrm{V})\}}\right) \\ &= \boxed{0.34\,\mathrm{A\,cm^{-2}}} \end{aligned}$$

(b) According to the Tafel equation

$$\begin{aligned} j &= j_0 e^{(1-\alpha)f\eta} \\ &= (2.5\times10^{-3}\,\mathrm{A\,cm^{-2}})e^{\{(1-0.58)\times(0.30\,\mathrm{V})/(0.025\,69\,\mathrm{V})\}} = \boxed{0.34\,\mathrm{A\,cm^{-2}}} \end{aligned}$$

The validity of the Tafel equation improves as the overpotential increases.

E25.20(b) The limiting current density is

$$j_{\mathrm{lim}} = \frac{zFDc}{\delta}$$

but the diffusivity is related to the ionic conductivity (Chapter 21)

$$D = \frac{\lambda RT}{z^2F^2} \quad \text{so} \quad j_{\mathrm{lim}} = \frac{c\lambda}{\delta zf}$$

$$\begin{aligned} j_{\mathrm{lim}} &= \frac{(1.5\,\mathrm{mol\,m^{-3}}) \times (10.60\times10^{-3}\,\mathrm{S\,m^2\,mol^{-1}}) \times (0.025\,69\,\mathrm{V})}{(0.32\times10^{-3}\,\mathrm{m}) \times (+1)} \\ &= \boxed{1.3\,\mathrm{A\,m^{-2}}} \end{aligned}$$

E25.21(b) For the iron electrode $E^{\ominus} = -0.44\,\mathrm{V}$ (Table 7.2) and the Nernst equation for this electrode (section 7.7a) is

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln\left(\frac{1}{[\mathrm{Fe}^{2+}]}\right) \qquad \nu = 2$$

Since the hydrogen overpotential is 0.60 V evolution of H_2 will begin when the potential of the Fe electrode reaches −0.60 V. Thus

$$-0.60\mathrm{V} = -0.44\mathrm{V} + \frac{0.025\,69\mathrm{V}}{2}\ln[\mathrm{Fe}^{2+}]$$

$$\ln[\mathrm{Fe}^{2+}] = \frac{-0.16\,\mathrm{V}}{0.0128\,\mathrm{V}} = -12.\bar{5}$$

$$[\mathrm{Fe}^{2+}] = \boxed{4 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}}$$

COMMENT. Essentially all Fe^{2+} has been removed by deposition before evolution of H_2 begins

E25.22(b) The zero-current potential of the electrode is given by the Nernst equation

$$E = E^{\ominus} - \frac{RT}{\nu F}\ln Q = E^{\ominus} - \frac{1}{f}\ln\frac{a\left(\mathrm{Fe}^{2+}\right)}{a\left(\mathrm{Fe}^{3+}\right)} = 0.77\,\mathrm{V} - \frac{1}{f}\ln\frac{a\left(\mathrm{Fe}^{2+}\right)}{a\left(\mathrm{Fe}^{3+}\right)}$$

The Butler–Volmer equation gives

$$j = j_0(\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta}) = j_0(\mathrm{e}^{(0.42)f\eta} - \mathrm{e}^{-0.58f\eta})$$

where η is the overpotential, defined as the working potential E' minus the zero-current potential E.

$$\eta = E' - 0.77\,\mathrm{V} + \frac{1}{f}\ln\frac{a\left(\mathrm{Fe}^{2+}\right)}{a\left(\mathrm{Fe}^{3+}\right)} = E' - 0.77\,\mathrm{V} + \frac{1}{f}\ln r,$$

where r is the ratio of activities; so

$$j = j_0(\mathrm{e}^{(0.42)E'/f}\mathrm{e}^{[(0.42)\times(-0.77\,\mathrm{V})/(0.025\,69\,\mathrm{V})]}r^{0.42}$$
$$-\,\mathrm{e}^{(-0.58)E'/f}\mathrm{e}^{\{(-0.58)\times(-0.77\,\mathrm{V})/(0.025\,69\,\mathrm{V})\}}r^{-0.58})$$

Specializing to the condition that the ions have equal activities yields

$$j = \boxed{(2.5\,\mathrm{mA\,cm^{-2}}) \times [(\mathrm{e}^{(0.42)E'/f} \times (3.4\bar{1} \times 10^{-6}) - \mathrm{e}^{(-0.58)E'/f} \times (3.5\bar{5} \times 10^{7})]}$$

E25.23(b) Note. The exercise did not supply values for j_0 or α. Assuming $\alpha = 0.5$, only j/j_0 is calculated. From Exercise 25.22(b)

$$j = j_0(\mathrm{e}^{(0.50)E'/f}\,\mathrm{e}^{-(0.50)E^{\ominus}/f}r^{0.50} - \mathrm{e}^{(-0.50)E'/f}\,\mathrm{e}^{(0.50)E^{\ominus}/f}\,r^{-0.50})$$
$$= 2j_0\sinh\left[\tfrac{1}{2}f\,E' - \tfrac{1}{2}f\,E^{\ominus} + \tfrac{1}{2}\ln r\right],$$

so, if the working potential is set at 0.50 V, then

$$j = 2j_0\sinh\left[\tfrac{1}{2}(0.91\,\mathrm{V})/(0.02569\,\mathrm{V}) + \tfrac{1}{2}\ln r\right]$$

$$j/j_0 = 2\,\sinh\left(8.4\bar{8} + \tfrac{1}{2}\ln r\right)$$

At $r = 0.1$: $j/j_0 = 2\sinh\left(8.4\bar{8} + \tfrac{1}{2}\ln 0.10\right) = 1.5 \times 10^3\,\mathrm{mA\,cm^{-2}} = \boxed{1.5\,\mathrm{A\,cm^{-2}}}$

At $r = 1$: $j/j_0 = 2\sinh(8.4\bar{8} + 0.0) = 4.8 \times 10^3\,\mathrm{mA\,cm^{-2}} = \boxed{4.8\,\mathrm{A\,cm^{-2}}}$

At $r = 10$: $j/j_0 = 2\sinh\left(8.4\bar{8} + \tfrac{1}{2}\ln 10\right) = 1.5 \times 10^4\,\mathrm{mA\,cm^{-2}} = \boxed{15\,\mathrm{A\,cm^{-2}}}$

E25.24(b) The potential needed to sustain a given current depends on the activities of the reactants, but the *over* potential does not. The Butler–Volmer equation says

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta})$$

This cannot be solved analytically for η, but in the high-overpotential limit it reduces to the Tafel equation

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \eta = \frac{1}{(1-\alpha)f}\ln\frac{j}{j_0} = \frac{0.025\,69\ \text{V}}{1-0.75}\ln\frac{15\ \text{mA cm}^{-2}}{4.0\times 10^{-2}\ \text{mA cm}^{-2}}$$

$$\eta = \boxed{0.61\ \text{V}}$$

This is a sufficiently large overpotential to justify use of the Tafel equation.

E25.25(b) The number of singly charged particles transported per unit time per unit area at equilibrium is the exchange current density divided by the charge

$$N = \frac{j_0}{e}$$

The frequency f of participation per atom on an electrode is

$$f = Na$$

where a is the effective area of an atom on the electrode surface.

For the Cu, $H_2|H^+$ electrode

$$N = \frac{j_0}{e} = \frac{1.0\times 10^{-6}\text{A cm}^{-2}}{1.602\times 10^{-19}\,\text{C}} = \boxed{6.2\times 10^{12}\ \text{s}^{-1}\text{cm}^{-2}}$$

$$f = Na = (6.2\times 10^{12}\text{s}^{-1}\ \text{cm}^{-2})\times(260\times 10^{-10}\,\text{cm})^2$$

$$= \boxed{4.2\times 10^{-3}\,\text{s}^{-1}}$$

For the $Pt|Ce^{4+}, Ce^{3+}$ electrode

$$N = \frac{j_0}{e} = \frac{4.0\times 10^{-5}\text{A cm}^{-2}}{1.602\times 10^{-19}\,\text{C}} = \boxed{2.5\times 10^{14}\ \text{s}^{-1}\ \text{cm}^{-2}}$$

The frequency f of participation per atom on an electrode is

$$f = Na = (2.5\times 10^{14}\,\text{s}^{-1}\ \text{cm}^{-2})\times(260\times 10^{-10}\text{cm})^2 = \boxed{0.17\,\text{s}^{-1}}$$

E25.26(b) The resistance R of an ohmic resistor is

$$R = \frac{\text{potential}}{\text{current}} = \frac{\eta}{jA}$$

where A is the surface area of the electrode. The overpotential in the low overpotential limit is

$$\eta = \frac{j}{fj_0} \quad \text{so} \quad R = \frac{1}{fj_0A}$$

(a) $R = \dfrac{0.025\,69\,\mathrm{V}}{(5.0\times10^{-12}\,\mathrm{A\,cm^{-2}})\times(1.0\,\mathrm{cm^2})} = 5.1\times10^{9}\,\Omega = \boxed{5.1\,\mathrm{G\Omega}}$

(b) $R = \dfrac{0.025\,69\,\mathrm{V}}{(2.5\times10^{-3}\,\mathrm{A\,cm^{-2}})\times(1.0\,\mathrm{cm^2})} = \boxed{10\,\Omega}$

E25.27(b) No reduction of cations to metal will occur until the cathode potential is dropped below the zero-current potential for the reduction of Ni^{2+} (-0.23 V at unit activity). Deposition of Ni will occur at an appreciable rate after the potential drops significantly below this value; however, the deposition of Fe will begin (albeit slowly) after the potential is brought below -0.44 V. If the goal is to deposit pure Ni, then the Ni will be deposited rather slowly at just above -0.44 V; then the Fe can be deposited rapidly by dropping the potential well below -0.44 V.

E25.28(b) As was noted in Exercise 25.18(a), an overpotential of 0.6 V or so is necessary to obtain significant deposition or evolution, so H_2 is evolved from acid solution at a potential of about -0.6 V. The reduction potential of Cd^{2+} is more positive than this (-0.40 V), so Cd will deposit (albeit slowly) from Cd^{2+} before H_2 evolution.

E25.29(b) Zn can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2}. The exchange current, according to the high negative overpotential limit, is

$$j = j_0 e^{-\alpha f \eta}$$

At the standard potential for reduction of Zn^{2+}(-0.76 V)

$$j = (0.79\,\mathrm{mA\,cm^{-2}})\times e^{-\{(0.5)\times(-0.76\,\mathrm{V})/(0.025\,69\,\mathrm{V})\}} = 2.1\times10^{9}\,\mathrm{mA\,cm^{-2}}$$

$\boxed{\text{much too large to allow deposition}}$. (That is, H_2 would begin being evolved, and fast, long before Zn began to deposit.)

E25.30(b) Fe can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2}. The exchange current, according to the high negative overpotential limit, is

$$j = j_0 e^{-\alpha f \eta}$$

At the standard potential for reduction of Fe^{2+}(-0.44 V)

$$j = (1\times10^{-6}\,\mathrm{A\,cm^{-2}})\times e^{-\{(0.5)\times(-0.44\,\mathrm{V})/(0.025\,69\,\mathrm{V})\}} = 5.2\times10^{-3}\,\mathrm{A\,cm^{-2}}$$

$\boxed{\text{a bit too large to allow deposition}}$. (That is, H_2 would begin being evolved at a moderate rate before Fe began to deposit.)

E25.31(b) The lead acid battery half-cells are

$$Pb^{4+} + 2e^- \rightarrow Pb^{2+} \qquad 1.67\,\mathrm{V}$$

and $$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \qquad -0.36\,\mathrm{V},$$

for a total of $E^{\ominus} = \boxed{2.03\,\text{V}}$. Power is

$$P = IV = (100 \times 10^{-3}\,\text{A}) \times (2.03\,\text{V}) = \boxed{0.203\,\text{W}}$$

if the cell were operating at its zero-current potential yet producing 100mA.

E25.32(b) Two electrons are lost in the corrosion of each zinc atom, so the number of zinc atoms lost is half the number of electrons which flow per unit time, i.e. half the current divided by the electron charge. The volume taken up by those zinc atoms is their number divided by number density; their number density is their mass density divided by molar mass times Avogadro's number. Dividing the volume of the corroded zinc over the surface from which they are corroded gives the linear corrosion rate; this affects the calculation by changing the current to the current density. So the rate of corrosion is

$$\begin{aligned}\text{rate} &= \frac{jM}{2e\rho N_A} = \frac{(2.0\,\text{A m}^{-2}) \times (65.39 \times 10^{-3}\,\text{kg mol}^{-1})}{2(1.602 \times 10^{-19}\,\text{C}) \times (7133\,\text{kg m}^{-3}) \times (6.022 \times 10^{23}\,\text{mol}^{-1})}\\ &= 9.5 \times 10^{-11}\,\text{m s}^{-1}\\ &= (9.5 \times 10^{-11}\,\text{m s}^{-1}) \times (10^3\text{mm m}^{-1}) \times (3600 \times 24 \times 365\,\text{s y}^{-1})\\ &= \boxed{3.0\ \text{mm y}^{-1}}\end{aligned}$$

Solutions to problems

Solutions to numerical problems

P25.2

$$\begin{aligned}Z_W &= \frac{p}{(2\pi mkT)^{1/2}}\ [25.1a]\\ &= \frac{p/Pa}{\left[(2\pi) \times (32.0) \times (1.6605 \times 10^{-27}\,\text{kg}) \times \left(1.381 \times 10^{-23}\,\text{J K}^{-1}\right)(300\,\text{K})\right]^{1/2}}\\ &= (2.69 \times 10^{22}\,\text{m}^{-2}\,\text{s}^{-1}) \times p/\text{Pa} = (2.69 \times 10^{18}\,\text{cm}^{-2}\,\text{s}^{-1}) \times p/\text{Pa}\end{aligned}$$

(a) At 100 kPa, $\boxed{Z_W = 2.69 \times 10^{23}\,\text{cm}^{-2}\ \text{s}^{-1}}$

(b) At 1.000 Pa, $\boxed{Z_W = 2.69 \times 10^{18}\,\text{cm}^{-2}\ \text{s}^{-1}}$

The nearest neighbor in titanium is 291 pm, so the number of atoms per cm^2 is approximately 1.4×10^{15} (the precise value depends on the details of the packing, which is hcp, and the identity of the surface). The number of collisions per exposed atom is therefore $Z_W/(1.4 \times 10^{15}\,\text{cm}^{-2})$.

(a) When $p = 100\,\text{kPa}$, $Z_{\text{atom}} = \boxed{2.0 \times 10^8\,\text{s}^{-1}}$

(b) When $p = 1.000\,\text{Pa}$, $Z_{\text{atom}} = \boxed{2.0 \times 10^3\,\text{s}^{-1}}$

P25.4 We follow Example 25.1 and draw up the following table (with pressures converted to Torr)

p/Torr	0.19	0.97	1.90	4.05	7.50	11.95
$(p/V)/(\text{Torr cm}^{-3})$	4.52	5.95	8.60	12.6	18.3	25.4

p/V is plotted against p in Figure 25.1.

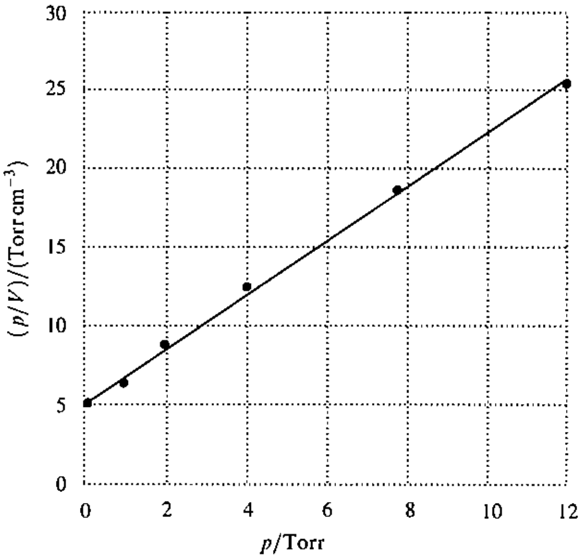


Figure 25.1

The low-pressure points fall on a straight line with intercept 4.7 and slope 1.8. It follows that $1/V_\infty = 1.8\,\text{Torr cm}^{-3}/\text{Torr} = 1.8\,\text{cm}^{-3}$, or $V_\infty = 0.57\,\text{cm}^3$ and $1/KV_\infty = 4.7\,\text{Torr cm}^{-3}$. Therefore,

$$K = \frac{1}{(4.7\,\text{Torr cm}^{-3}) \times (0.57\,\text{cm}^3)} = \boxed{0.37\,\text{Torr}^{-1}} = \boxed{0.0028\,\text{Pa}^{-1}}$$

COMMENT. It is unlikely that low-pressure data can be used to obtain an accurate value of the volume corresponding to complete coverage. See Problem 25.6 for adsorption data at higher pressures.

P25.6 We assume that the data fit the Langmuir isotherm; to confirm this we plot p/V against p and expect a straight line [Example 25.1]. We draw up the following table

p/atm	0.050	0.100	0.150	0.200	0.250
$p/V/(10^{-2}\text{atm cm}^{-3})$	4.1	7.52	11.5	14.7	17.9

The data are plotted in Figure 25.2.

They fit closely to a straight line with slope 0.720 dm^{-3}. Hence

$$V_\infty = \boxed{1.3\bar{9}\,\text{cm}^{-3}} = 1.3\bar{9} \times 10^{-3}\,\text{dm}^{-3} \approx V_{\text{mon}}$$

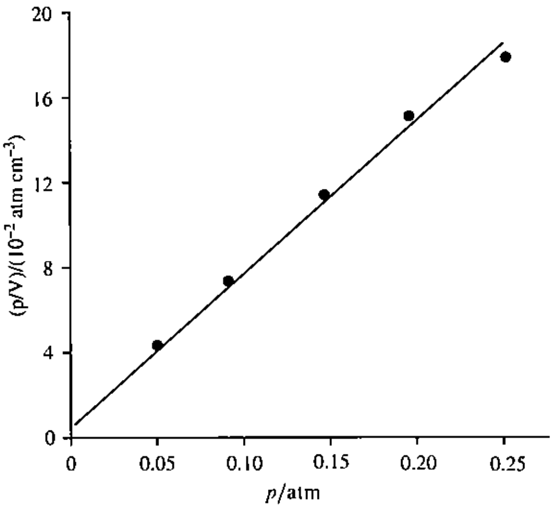


Figure 25.2

The number of H_2 molecules corresponding to this volume is

$$N_{H_2} = \frac{pVN_A}{RT} = \frac{(1.00\,\text{atm}) \times (1.3\bar{9} \times 10^{-3}\,\text{dm}^3) \times (6.02 \times 10^{23}\,\text{mol}^{-1}))}{(0.0821\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})} = 3.73 \times 10^{19}$$

The area occupied is the number of molecules times the area per molecule. The area per molecule can be estimated from the density of the liquid

$$A = \pi\left(\frac{3V}{4\pi}\right)^{2/3} \quad \left[V = \text{volume of molecule} = \frac{M}{\rho N_A}\right]$$

$$= \pi\left(\frac{3M}{4\pi\rho N_A}\right)^{2/3} = \pi\left(\frac{3 \times (2.02\,\text{g}\,\text{mol}^{-1})}{4\pi \times (0.0708\,\text{g}\,\text{cm}^{-3}) \times (6.02 \times 10^{23}\,\text{mol}^{-1})}\right)^{2/3}$$

$$= 1.58 \times 10^{-15}\text{cm}^2$$

Area occupied $= (3.73 \times 10^{19}) \times (1.58 \times 10^{-15}\,\text{cm}^2) = (5.9 \times 10^4\,\text{cm}^2) = \boxed{5.9\,\text{m}^2}$

COMMENT. The value for V_∞ calculated here may be compared to the value obtained in Problem 25.4. The agreement is not good and illustrates the point that these kinds of calculations provide only rough value surface areas.

P25.8 We assume that the Langmuir isotherm applies.

$$\theta = \frac{Kp}{1 + Kp}\ [25.4] \quad \text{and} \quad 1 - \theta = \frac{1}{1 + Kp}$$

For a strongly adsorbed species, $Kp \gg 1$ and $1 - \theta = 1/Kp$. Since the reaction rate is proportional to the pressure of ammonia and the fraction of sites left uncovered by the strongly adsorbed hydrogen product, we can write

$$\frac{dp_{NH_3}}{dt} = -k_c p_{NH_3}(1 - \theta) \approx -\boxed{\frac{k_c p_{NH_3}}{K p_{H_2}}}$$

To solve the rate law, we write

$$p_{H_2} = \tfrac{3}{2}\{p_{0NH_3} - p_{NH_3}\} \quad \left[NH_3 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2\right]$$

from which it follows that, with $p = p_{NH_3}$

$$\frac{-dp}{dt} = \frac{kp}{p_0 - p}, \quad k = \frac{2k_c}{3K}$$

This equation integrates as follows

$$\int_{p_0}^{p}\left(1 - \frac{p_0}{p}\right) dp = k\int_0^t dt$$

or $\boxed{\dfrac{p - p_0}{t} = k + \dfrac{p_0}{t}\ln\dfrac{p}{p_0}}$

We write $F' = (p_0/t)\ln(p/p_0)$, $G = (p - p_0)/t$

and obtain $G = k + F' = p_0F$

Hence, a plot of G against F' should give a straight line with intercept k at $F' = 0$. Alternatively, the difference $G - F'$ should be a constant, k. We draw up the following table (with pressures converted to Torr)

t/s	0	30	60	100	160	200	250
p/Torr	100	88	84	80	77	74	72
$G/(\text{Torr s}^{-1})$		−0.40	−0.27	−0.20	−0.14	−0.13	−0.11
$F'/(\text{Torr s}^{-1})$		−0.43	−0.29	−0.22	−0.16	−0.15	−0.13
$(G - F')/(\text{Torr s}^{-1})$		0.03	0.02	0.02	0.02	0.02	0.02

Thus, the data fit the rate law, and we find $\boxed{k = 0.02\ \text{Torr s}^{-1}} = \boxed{0.05\ \text{kPa s}^{-1}}$.

P25.10 Application of the van't Hoff equation [25.7] to adsorption equilibria yields

$$\left(\frac{\partial \ln K}{\partial T}\right)_\theta = \frac{-\Delta_{ad}H^\ominus}{RT^2} \quad \text{or} \quad \left(\frac{\partial \ln K}{\partial(1/T)}\right)_\theta = \frac{-\Delta_{ad}H^\ominus}{R}$$

Hence, a plot (Figure 25.3) of $\ln K$ against $1/T$ should be a straight line with slope $-\Delta_{ad}H^\ominus/R$. The transformed data and plot follow

T/K	28.3	298	308	318
$10^{-11}K$	2.642	2.078	1.286	1.085
1000 K/T	3.53	3.36	3.25	3.14
$\ln K$	26.30	26.06	25.58	25.41

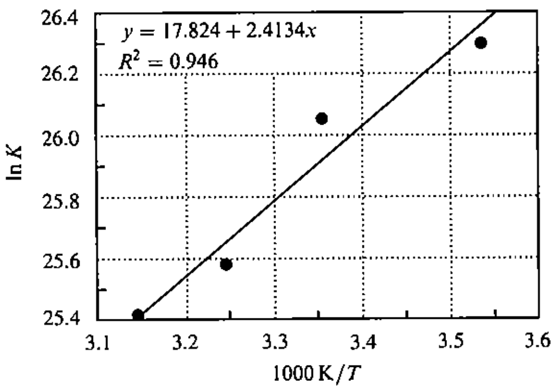


Figure 25.3

The plot is not the straightest of lines. Still, we can extract

$$-\Delta_{\rm ad}H^\ominus = -(8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}) \times (2.41 \times 10^3\,\text{K})$$

$$= -20.0 \times 10^3\,\text{J mol}^{-1} = \boxed{-20.1\,\text{kJ mol}^{-1}}$$

The Gibbs energy for absorption is

$$-\Delta_{\rm ad}G^\ominus = -\Delta_{\rm ad}H^\ominus - T\Delta_{\rm ad}S^\ominus = -20.1\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (0.146\,\text{kJ mol}^{-1}\,\text{K}^{-1})$$

$$= \boxed{63.6\,\text{kJ mol}^{-1}}$$

P25.12 For the Langmuir adsorption isotherm we must alter eqn 25.4 so that it describes adsorption from solution. This can be done with the transforms

$p \to$ concentration, c

$V \to$ amount adsorbed per gram adsorbent, s

Langmuir isotherm and regression analysis:

$$\frac{c}{s} = \frac{c}{s_\infty} + \frac{1}{Ks_\infty}$$

$$\frac{1}{s_\infty} = 0.163\,\text{g mmol}^{-1}, \text{standard deviation} = 0.017\,\text{g mmol}^{-1}$$

$$\frac{1}{Ks_\infty} = 35.6\,(\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1}),$$

standard deviation $= 5.9(\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1})$

$\boxed{R\ (\text{Langmuir}) = 0.973}$

$$K = \frac{0.163\,\text{g mmol}^{-1}}{35.6(\text{mmol dm}^{-3}) \times (\text{g mmol}^{-1})} = 0.0046\,\text{dm}^3\,\text{mmol}^{-1}$$

Freundlich isotherm and regression analysis:

$$s = c_1 c^{1/c_2}$$

$$c_1 = 0.139, \quad \text{standard deviation} = 0.012$$

$$\frac{1}{c_2} = 0.539, \quad \text{standard deviation} = 0.003$$

$$\boxed{R \text{ (Freundlich)} = 0.999\,94}$$

Temkin isotherm and regression analysis:

$$s = c_1 \ln(c_2 c)$$

$$c_1 = 1.08, \quad \text{standard deviation} = 0.14$$

$$c_2 = 0.074, \quad \text{standard deviation} = 0.023$$

$$\boxed{R \text{ (Temkin)} = 0.9590}$$

The correlation coefficients and standard deviations indicate that the $\boxed{\text{Freundlich isotherm}}$ provides the best fit of the data.

P25.14 $E = E^\ominus + (RT/zF)\ln a(M^+)$

Deposition may occur when the potential falls to below E and so simultaneous deposition will occur if the two potentials are the same; hence the relative activities are given by

$$E^\ominus(\mathrm{Sn}, \mathrm{Sn}^{2+}) + \frac{RT}{2F}\ln a(\mathrm{Sn}^{2+}) = E^\ominus(\mathrm{Pb}, \mathrm{Pb}^{2+}) + \frac{RT}{2F}\ln a(\mathrm{Pb}^{2+})$$

$$\text{or } \ln\frac{a(\mathrm{Sn}^{2+})}{a(\mathrm{Pb}^{2+})} = \left(\frac{2F}{RT}\right)\{E^\ominus(\mathrm{Pb}, \mathrm{Pb}^{2+}) - E^\ominus(\mathrm{Sn}, \mathrm{Sn}^{2+})\} = \frac{(2)\times(-0.126+0.136)\,\mathrm{V}}{0.0257\,\mathrm{V}} = 0.78$$

That is, we require $\boxed{a(\mathrm{Sn}^{2+}) \approx 2.2a(\mathrm{Pb}^{2+})}$

P25.16 $E' = E - IR_s - \dfrac{2RT}{zF}\ln g(I)$ [25.64a]

$$g = \frac{(I/A\bar{j})^{2z}}{\left[\left(1 - (I/Aj_{\mathrm{lim,L}})\right)\times\left(1 - (I/Aj_{\mathrm{lim,R}})\right)\right]^{1/2}}$$

with $j_{\mathrm{lim}} = cRT\lambda/zF\delta$ [25.57b] $= a\lambda$

$$R_s = \frac{l}{\kappa A} = \frac{l}{cA\Lambda_m} \text{ with } \Lambda_m = \lambda_+ + \lambda_-$$

Therefore, $E' = E - \dfrac{Il}{cA\Lambda_m} - \dfrac{2RT}{zF}\ln g(I)$

$$\text{with } g(I) = \frac{\left(I^2/A^2 j_{\mathrm{LO}} j_{\mathrm{RO}}\right)^z}{\left[1 - (I/Aa_{\mathrm{L}}\lambda_{\mathrm{L+}})\right]^{1/2}\left[1 - (I/Aa_{\mathrm{R}}\lambda_{\mathrm{R+}})\right]^{1/2}}$$

with $a_{\mathrm{L}} = RTc_{\mathrm{L}}/z_{\mathrm{L}}F\delta_{\mathrm{L}}$ and $a_{\mathrm{R}} = RTc_{\mathrm{R}}/z_{\mathrm{R}}F\delta_{\mathrm{R}}$

For the cell Zn|ZnSO$_4$(aq)||CuSO$_4$(aq)|Cu, $l = 5\,\text{cm}$, $A = 5\,\text{cm}^2$, $c(\text{M}_\text{L}^+) = c(\text{M}_\text{R}^+) = 1\,\text{mol dm}^{-3}$, $z_\text{L} = z_\text{R} = 2$, $\lambda_{\text{L}+} = 107\,\text{S cm}^2\,\text{mol}^{-1}$, $\lambda_{\text{R}+} = 106\,\text{S cm}^2\,\text{mol}^{-1} \approx \lambda_{\text{L}+}$, $\lambda_- = \lambda_{\text{SO}_4^{2-}} = 160\,\text{S cm}^{-2}\text{mol}^{-1}$. $\Lambda_\text{m} \approx (107+160)\,\text{S cm}^2\text{mol}^{-1} = 267\,\text{S cm}^2\,\text{mol}^{-1}$ for both electrolyte solutions. We take $\delta \approx 0.25\,\text{mm}$ [25.57b] and $j_\text{LO} \approx j_\text{RO} \approx 1\,\text{mA cm}^{-2}$. We can also take

$$E^\ominus(a \approx 1) = E^\ominus(\text{Cu},\text{Cu}^{2+}) - E^\ominus(\text{Zn},\text{Zn}^{2+}) = [0.34 - (-0.76)]\,\text{V} = 1.10\,\text{V}$$

$$R_\text{s} = \frac{5\,\text{cm}}{(1\,\text{M}) \times (267\,\text{S cm}^2\,\text{mol}^{-1}) \times (5\,\text{cm}^2)} = 3.\bar{8}\,\Omega$$

$$j_\text{lim} = j_\text{lim}^+ = \frac{1}{2} \times \left(\frac{(0.0257\,\text{V}) \times (107\,\text{S cm}^2\,\text{mol}^{-1}) \times (1\,\text{M})}{0.25 \times 10^{-3}\,\text{m}}\right) \approx 5.5 \times 10^{-2}\,\text{S V cm}^{-2}$$

$$= 5.5 \times 10^{-2}\,\text{A cm}^{-2}$$

If follows that

$$E'/\text{V} = (1.10) - 3.7\bar{5}(I/\text{A}) - (0.0257)\ln\left(\frac{(I/5 \times 10^{-3}\,\text{A})^4}{1 - 3.6(I/\text{A})}\right)$$

$$= (1.10) - 3.7\bar{5}(I/\text{A}) - (0.0257)\ln\left(\frac{1.6 \times 10^9(I/\text{A})^4}{1 - 3.6(I/\text{A})}\right)$$

This function is plotted in Figure 25.4.

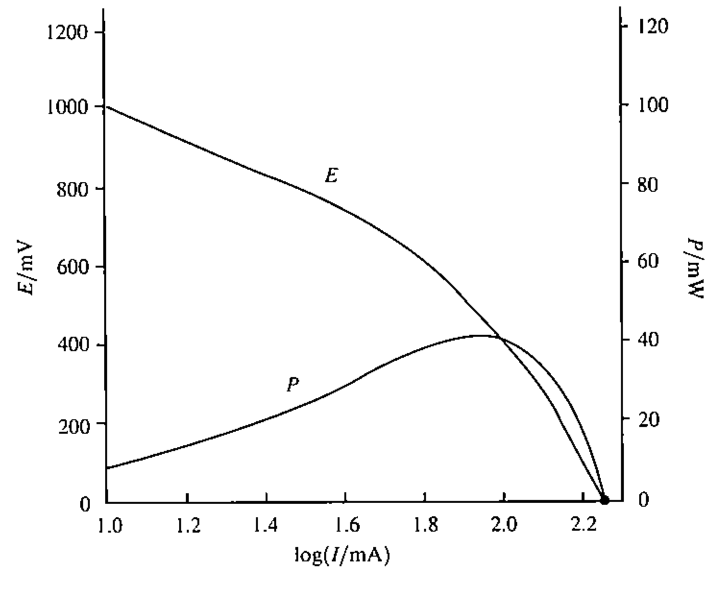


Figure 25.4

The power is

$$P = IE'$$

and so $$P/\text{W} = 1.10(I/\text{A}) - 3.7\bar{5}(I/\text{A})^2 - 0.0257(I/\text{A})\ln\left(\frac{1.6 \times 10^9(I/\text{A})^4}{1 - 3.6(I/\text{A})}\right)$$

This function is also plotted in Figure 25.4. Maximum power is delivered at about $\boxed{87\,\text{mA}}$ and 0.46 V and is about 40 mW.

P25.18 $Fe^{2+} + 2e^- \rightarrow Fe$ $\nu = 2$; $E^\ominus = -0.447$

(a)

$$E_0 = E^\ominus - \frac{RT}{\nu F}\ln Q \quad [7.29]$$

$$= E^\ominus - \frac{RT}{\nu F}\frac{1}{Fe^{2+}} \text{ assuming } \gamma_{Fe^{2+}} = 1$$

$$= -0.447\,\text{V} - \frac{25.693 \times 10^{-3}\,\text{V}}{2}\ln\left(\frac{\text{mol dm}^{-3}}{1.70 \times 10^{-6}\,\text{mol dm}^{3}}\right)$$

$$\boxed{E_0 = -0.618\,\text{V}}$$

$$\eta = E' - E_0 \; [25.39]$$

η values are reported in the table below.

(b)

$$j = \frac{\nu F}{A}\frac{dn_{Fe}}{dt} = \frac{2\,(96485\,\text{C mol}^{-1})}{9.1\,\text{cm}^2}\frac{dn_{Fe}}{dt}$$

$$j = j_0\left(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right) = j_0 e^{-\alpha f\eta}\{e^{f\eta} - 1\}$$

$$= -j_c\{e^{f\eta} - 1\} \; [25.40, 25.41]$$

$$j_c = \frac{-j}{e^{f\eta} - 1}$$

j_c values are reported in the following table

$dn_{Fe}/dt\,(10^{-12}\,\text{mol s}^{-1})$	$-E'/\text{mV}$	$-\eta/\text{mV}$	$j/(\mu\text{A cm}^{-12})$	$jc/(\mu\text{A cm}^{-12})$
1.47	702	84	0.0312	0.0324
2.18	727	109	0.0462	0.0469
3.11	752	134	0.0659	0.0663
7.26	812	194	0.154	0.154

(c)

$$j_c = j_0 e^{-\alpha f\eta} \; [25.40]$$

$$\ln j_c = \ln j_0 - \alpha f\eta$$

Performing a linear regression analysis of the $\ln j_c$ versus η data, we find

$\ln j_0 = 4.608$, standard devation $= 0.015$

$\alpha f = 0.0413\text{mV}$, standard devation $= 0.000\,11$

$$\boxed{R = 0.999\,94}$$

The correlation coefficient and the standard deviation indicate that the plot provides an excellent description of the data

$$j_0 = e^{4.608} \quad \text{or} \quad j_0 = 0.00997\,\mu\text{A cm}^{-2}$$

$$\alpha = \frac{0.01413}{f} = (0.01413\,\text{mV}^{-1}) \times (26.693\,\text{mV})$$

$$\boxed{\alpha = 0.363}$$

P25.20 This problem differs somewhat from the simpler one-electron transfers considered in the text. In place of $Ox + e^- \rightarrow Red$ we have here

$$In^{3+} + 3e^- \rightarrow In$$

namely, a three-electron transfer. Therefore eqns 25.33a, 25.33b, and all subsequent equations including the Butler–Volmer equation [25.41] and the Tafel equations [25.44–25.46] need to be modified by including the factor z (in this case 3) in the equation. Thus, in the place of eqn 25.33b, we have

$$\Delta^{\ddagger}G_c = \Delta^{\ddagger}G_c(0) + z\alpha F\Delta\phi$$

and in place of eqns 25.45 and 25.47

$$\ln j = \ln j_0 + z(1-\alpha)f\eta \quad \text{anode}$$
$$\ln(-j) = \ln j_0 - z\alpha f\eta \quad \text{cathode}$$

We draw up the following table

$j/(\mathrm{A\,m^{-2}})$	$-E/\mathrm{V}$	η/V	$\ln(j/\mathrm{A\,m^{-2}})$
0	0.388	0	
0.590	0.365	0.023	−0.5276
1.438	0.350	0.038	0.3633
3.507	0.335	0.053	1.255

We now do a linear regression of $\ln j$ against η with the following results (see Figure 25.5)

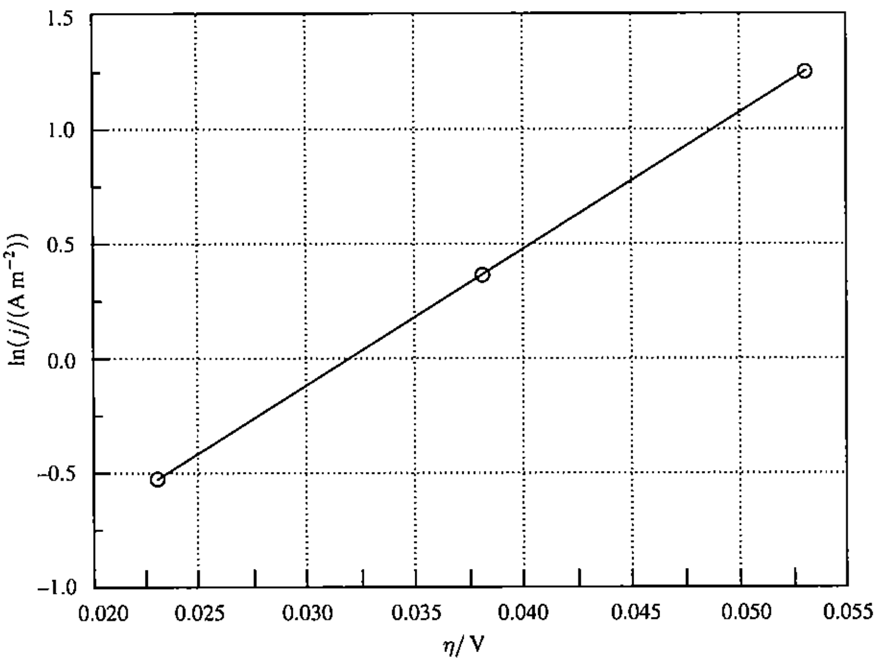


Figure 25.5

$z(1-\alpha)f = 59.42\ \mathrm{V^{-1}}$, standard deviation $= 0.0154$

$\ln j_0 = -1.894$, standard deviation $= 0.0006$

$R = 1$ (almost exact)

Thus, although there are only three data points, the fit to the Tafel equation is almost exact. Solving for α from $z(1-\alpha)f = 59.42\ \mathrm{V^{-1}}$, we obtain

$$\alpha = 1 - \frac{59.42\ \mathrm{V^{-1}}}{3f} = 1 - \left(\frac{59.42\ \mathrm{V^{-1}}}{3}\right) \times (0.025\,262\ \mathrm{V})$$
$$= 0.49\overline{96} = \boxed{0.50}$$

which matches the usual value of α exactly.

$$j_0 = \mathrm{e}^{-1.894} = \boxed{0.150\ \mathrm{A\ m^{-2}}}$$

The cathodic current density is obtained from

$$\ln(-j_c) = \ln j_0 - z\alpha f\eta \quad \eta = 0.023\ \mathrm{V\ at} - E/\mathrm{V} = 0.365$$
$$= -1.894 - (3 \times 0.49\overline{96} \times 0.023)/(0.025\,262)$$
$$= -3.2\overline{59}$$

$$-j_c = \mathrm{e}^{-3.2\overline{59}} = 0.038\bar{4}\ \mathrm{A\ m^{-2}}$$

$$-j_c = \boxed{0.038\bar{4}\ \mathrm{A\ m^{-2}}}$$

P25.22 At large positive values of the overpotential the current density is anodic.

$$j = j_0\left[\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta}\right] \quad [25.41]$$
$$\approx j_0\mathrm{e}^{(1-\alpha)f\eta} = j_a \quad [25.40]$$
$$\ln j = \ln j_0 + (1-\alpha)f\eta$$

Performing a linear regression analysis of $\ln j$ against η, we find

$\ln(j_0/(\mathrm{mA\ m^{-2}})) = -10.826$, standard deviation $= 0.287$

$(1-\alpha)f = 19.550\ \mathrm{V^{-1}}$, standard deviation $= 0.355$

$\boxed{R = 0.999\,01}$

$$j_0 = \mathrm{e}^{-10.826}\ \mathrm{mA\ m^{-2}} = \boxed{2.00 \times 10^{-5}\ \mathrm{mA\ m^{-2}}}$$

$$\alpha = 1 - \frac{19.550\ \mathrm{V^{-1}}}{f} = 1 - \frac{19.550\ \mathrm{V^{-1}}}{(0.025\,693\ \mathrm{V})^{-1}}$$

$\boxed{\alpha = 0.498}$

The linear regression explains 99.90 percent of the variation in a $\ln j$ against η plot and standard deviations are low. There are $\boxed{\text{no}}$ deviations from the Tafel equation/plot.

Solutions to theoretical problems

P25.24 A general change in the Gibbs function of a one-component system with a surface is

$$dG = -S\,dT + V\,dp + \gamma\,d\sigma + \mu\,dn$$

Let $G = G(g) + G(\sigma)$ and $n = n(g) + n(\sigma)$; then

$$dG(g) = -S(g)\,dT + V(g)\,dp + \mu(g)\,dn(g)$$

$$dG(\sigma) = -S(\sigma)\,dT + \gamma\,d\sigma + \mu(\sigma)\,dn(\sigma)$$

At equilibrium, $\mu(\sigma) = \mu(g) = \mu$. At constant temperature, $dG(\sigma) = \gamma\,d\sigma + \mu\,dn(\sigma)$. Since dG is an exact differential, this expression integrates to

$$G(\sigma) = \gamma\sigma + \mu n(\sigma)$$

Therefore, $dG(\sigma) = \sigma\,d\gamma + \gamma\,d\sigma + \mu\,dn(\sigma) + n(\sigma)\,d\mu$
But since $dG(\sigma) = \gamma\,d(\sigma) + \mu\,dn(\sigma)$ we conclude that $\sigma\,d\gamma + n(\sigma)\,d\mu = 0$
Since $d\mu = RT\,d\ln p$, this relation is equivalent to

$$n(\sigma) = -\frac{\sigma\,d\gamma}{d\mu} = -\left(\frac{\sigma}{RT}\right) \times \left(\frac{d\gamma}{d\ln p}\right)$$

Now express $n(\sigma)$ as an adsorbed volume using

$$n(\sigma) = \frac{p^{\ominus}V_a}{RT^{\ominus}}$$

and express $d\gamma$ as a kind of chemical potential through

$$d\mu' = \frac{RT^{\ominus}}{p^{\ominus}}d\gamma$$

evaluated at a standard temperature and pressure ($T^{\ominus}$ and $p^{\ominus}$), then

$$\boxed{-\left(\frac{\sigma}{RT}\right) \times \left(\frac{d\mu'}{d\ln p}\right) = V_a}$$

P25.26

$$\theta = \frac{Kp}{1+Kp}, \quad \theta = \frac{V}{V_\infty}$$

$$p = \frac{\theta}{K(1-\theta)} = \frac{V}{K(V_\infty - V)}$$

$$\frac{dp}{dV} = \frac{1}{K(V_\infty - V)} + \frac{V}{K(V_\infty - V)^2} = \frac{V_\infty}{K(V_\infty - V)^2}$$

$$d\mu' = -\left(\frac{RT}{\sigma}\right) V\,d\ln p = \frac{-RT}{p\sigma}V\,dp$$

$$= -\left(\frac{RT}{\sigma}\right)\left(\frac{K(V_\infty - V)}{V}\right) V \left(\frac{V_\infty}{K(V_\infty - V)^2}\right) dV$$

$$= -\left(\frac{RT}{\sigma}\right)\left(\frac{V_\infty\,dV}{V_\infty - V}\right)$$

Therefore, we can adopt any of several forms,

$$\mathrm{d}\mu' = -\frac{((RT/\sigma)V_\infty)}{V_\infty - V}\mathrm{d}V = -\frac{(RT/\sigma)}{1-\theta}\mathrm{d}V = -\frac{(RTV_\infty/\sigma)}{1-\theta}\mathrm{d}\theta = \boxed{\left(\frac{RTV_\infty}{\sigma}\right)\mathrm{d}\ln(1-\theta)}$$

P25.28

$$j = j_0\{\mathrm{e}^{(1-\alpha)f\eta} - \mathrm{e}^{-\alpha f\eta}\}\ [25.41]$$

$$= j_0\left\{1 + (1-\alpha)\eta f + \tfrac{1}{2}(1-\alpha)^2\eta^2 f^2 + \cdots - 1 + \alpha f\eta - \tfrac{1}{2}\alpha^2\eta^2 f^2 + \cdots\right\}$$

$$= j_0\left\{\eta f + \tfrac{1}{2}(\eta f)^2(1-2\alpha) + \cdots\right\}$$

$$\langle j\rangle = j_0\left\{\langle\eta\rangle f + \tfrac{1}{2}(1-2\alpha)f^2\langle\eta^2\rangle + \cdots\right\}$$

$$\langle\eta\rangle = 0, \text{ because } \frac{\omega}{2\pi}\int_0^{2\pi/\omega}\cos\omega t\,\mathrm{d}t = 0 \quad \left[\frac{2\pi}{\omega}\text{is the period}\right]$$

$$\left\langle\eta^2\right\rangle = \tfrac{1}{2}\eta_0^2, \text{ because } \frac{\omega}{2\pi}\int_0^{2\pi/\omega}\cos^2\omega t\,\mathrm{d}t = \tfrac{1}{2}$$

Therefore, $\boxed{\langle j\rangle = \tfrac{1}{4}(1-2\alpha)f^2 j_0\eta_0^2}$

and $\langle j\rangle = 0$ when $\alpha = \tfrac{1}{2}$. For the mean current,

$$\langle I\rangle = \tfrac{1}{4}(1-2\alpha)f^2 j_0 S\eta_0^2$$

$$= \tfrac{1}{4}\times(1-0.76)\times\left(\frac{(7.90\times10^{-4}\,\mathrm{A\,cm^{-2}})\times(1.0\,\mathrm{cm^2})}{(0.0257\,\mathrm{V})^2}\right)\times(10\,\mathrm{mV})^2$$

$$= \boxed{7.2\,\mu A}$$

P25.30

$$j = \left(\frac{cFD}{\delta}\right) \times (1 - \mathrm{e}^{f\eta^c})\ [29.51;\ z = 1] = \boxed{j_L\left(1 - \mathrm{e}^{F\eta^c/RT}\right)}$$

The form of this expression is illustrated in Figure 25.6.

For the anion current, the sign of η^c is changed, and the current of anions approaches its limiting value as η^c becomes more positive (Figure 25.6).

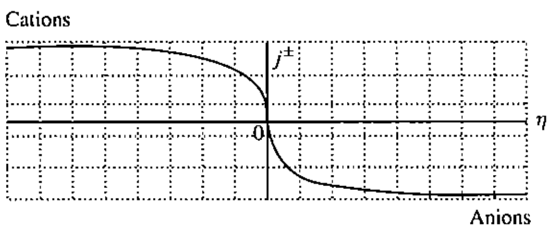


Figure 25.6

Solutions to applications

P25.32 Equilibrium constants vary with temperature according to the van't Hoff equation [7.25] which can be written in the form

$$\frac{K_1}{K_2} = e^{-\left[(\Delta_{ad}H^{\ominus}/R)((1/T_1)-(1/T_2))\right]}$$

or

$$\frac{K_1}{K_2} = \exp\left[\frac{160\times 10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{673\,\mathrm{K}} - \frac{1}{773\,\mathrm{K}}\right)\right] = \boxed{40.4}$$

As measured by the equilibrium constant of absorption, NO is about 40 times more strongly absorbed at 500 °C than at 400 °C.

P25.34 **(a)** $q_{\text{water}} = k(\text{RH})^{1/n}$

With a power law regression analysis we find

$\boxed{k = 0.2289}$, standard deviation = 0.0068

$1/n = 1.6182$, standard deviation = 0.0093; $\boxed{n = 0.6180}$

$R = 0.999\,508$

A linear regression analysis may be performed by transforming the equation to the following form by taking the logarithm of the Freundlich type equation

$$\ln q_{\text{water}} = \ln k + \frac{1}{n}\ln(\text{RH})$$

$\ln k = -1.4746$, standard deviation = 0.0068; $\boxed{k = 0.2289}$

$\frac{1}{n} = 1.6183$, standard deviation = 0.0093; $\boxed{n = 0.6180}$

$R = 0.999\,508$

The two methods give exactly the same result because the software package for performing the power law regression performs the transformation to linear form for you. Both methods are actually performing a linear regression.

The correlation coefficient indicates that 99.95 percent of the data variation is explained with the Freundlich type isotherm. The Freundlich fit hypothesis looks very good.

(b) The Langmuir isotherm model describes adsorption sites that are independent and equivalent. This assumption seems to be valid for the VOC case in which molecules interact very weakly. However, water molecules interact much more strongly through forces such as hydrogen bonding and multilayers may readily form at the lower temperatures. The intermolecular forces of water apparently cause adsorption sites to become nonequivalent and dependent. In this particular case the Freundlich type isotherm becomes the better description.

(c) $r_{\text{VOC}} = 1 - q_{\text{water}}$ where $r_{\text{VOC}} \equiv q_{\text{VOC}}/q_{\text{VOC,RH}=0}$

$r_{\text{VOC}} = 1 - k(\text{RH})^{1/n}$

$1 - r_{\text{VOC}} = k(\text{RH})^{1/n}$

To determine the goodness-of-fit, k, and n we perform a power law regression fit of $1 - r_{\mathrm{VOC}}$ against RH. Results are

$$\boxed{k = 0.5227}, \quad \text{standard deviation} = 0.0719$$

$$\frac{1}{n} = 1.3749, \quad \text{standard deviation} = 0.0601; \quad \boxed{n = 0.7273}$$

$$R = 0.99620$$

Since 99.62 percent of the variation is explained by the regression, we conclude that the hypothesis that $r_{\mathrm{VOC}} = 1 - q_{\mathrm{water}}$ may be very useful. The values of R and n differ significantly from those of part (a). It may be that water is adsorbing to some portions of the surface and VOC to others.

P25.36 $$E^{\ominus} = \frac{-\Delta_r G^{\ominus}}{\nu F}$$

(a) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \quad \Delta_r G^{\ominus} = -237\ \mathrm{kJ\ mol^{-1}}$

Since $\nu = 2$,

$$E^{\ominus} = \frac{-(-237\ \mathrm{kJ\ mol^{-1}})}{(2) \times (96.48\ \mathrm{kC\ mol^{-1}})} = \boxed{+1.23\ \mathrm{V}}$$

(b) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$$\Delta_r G^{\ominus} = 2\Delta_f G^{\ominus}(H_2O) + \Delta_f G^{\ominus}(CO_2) - \Delta_f G^{\ominus}(CH_4)$$

$$= [(2) \times (-237.1) + (-394.4) - (-50.7)]\ \mathrm{kJ\ mol^{-1}} = -817.9\ \mathrm{kJ\ mol^{-1}}$$

As written, the reaction corresponds to the transfer of eight electrons. It follows that, for the species in their standard states,

$$E^{\ominus} = \frac{-(-817.9\ \mathrm{kJ\ mol^{-1}})}{(8) \times (96.48\ \mathrm{kC\ mol^{-1}})} = \boxed{+1.06\ \mathrm{V}}$$

P25.38 $$I_{\mathrm{corr}} = \bar{A}\bar{j}_0 e^{fE/4} \quad [25.66]$$

with $E = -0.62 - (-0.94)\ \mathrm{V} = 0.32\ \mathrm{V}$ [as in Problem 25.37]

$$I_{\mathrm{corr}} \approx (0.25 \times 10^{-6}\ \mathrm{A}) \times (e^{0.32/4 \times 0.0257}) \approx \boxed{6\ \mu\mathrm{A}}$$