

## 26 The kinetics of complex reactions

### Solutions to exercises

#### Discussion questions

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- E26.1(b)** 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

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

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 26.4 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:

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

where  $k = 1/2 k_p(fk_i k_t)^{-1/2}$ , 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.

- E26.2(b)** Refer to eqns 26.26 and 26.27, which are the analogues of the Michaelis–Menten and Lineweaver–Burk equations (26.21 and 26.22), as well as to Fig. 26.12. There are three major modes of inhibition that give rise to distinctly different kinetic behaviour (Fig. 26.12). 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  $\alpha$  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  $\alpha'$  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 26.12c 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 26.27), the mode of inhibition, the values of  $\alpha$  or  $\alpha'$ , and the values of  $K_I$ , or  $K_I'$  may be obtained.

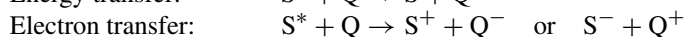
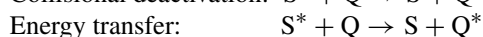
**E26.3(b)** The steady-state approximation is applied to reactive intermediates in consecutive reactions and is the assumption that their concentrations do not change much with time. It is a good approximation if the rate constant for the reaction of the intermediate, in either the forward or backward direction, is large compared to the rate constant in the other direction. This approximation is applicable when chemical production and chemical consumption are closely balanced.

In the steady-state condition of a chemical reaction, a reactant or product is maintained at a constant concentration throughout the course of the reaction by supplying it to or withdrawing it from the reaction vessel. Steady-states are not equilibrium states in the thermodynamic sense and in fact are the other extreme from equilibrium.

Bistability is a condition in which two distinct, far from equilibrium, steady-states are chemically available to the reacting system. In some systems, bistability is a necessary condition for chemical oscillation to occur. Under the right conditions, the system may jump periodically between the two steady states as the reaction progresses. Refer to Figs 26.19 and 26.20 of the text for an illustration of the process. However, bistability alone is not a sufficient condition to achieve oscillation in an auto-catalytic reaction. In order for the oscillation to occur, it is necessary to have a feedback mechanism involving a third species Z that reacts with the intermediates X and Y according to:  $Y + Z \rightarrow X$  and  $X + Z \rightarrow Y$ . Thus Z reacts with X to produce Y and with Y to produce X. As a result the system can switch periodically between the upper and lower steady states.

**E26.4(b)** 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 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 17.7e). 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.

### Numerical exercises

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

**E26.5(b)** The intermediates are NO and NO<sub>3</sub> and we apply the steady-state approximation to each of their concentrations

$$k_2[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{N}_2\text{O}_5] = 0$$

$$k_1[\text{N}_2\text{O}_5] - k'_1[\text{NO}_2][\text{NO}_3] - k_2[\text{NO}_2][\text{NO}_3] = 0$$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt}$$

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + k'_1[\text{NO}_2][\text{NO}_3] - k_3[\text{NO}][\text{N}_2\text{O}_5]$$

From the steady state equations

$$k_3[\text{NO}][\text{N}_2\text{O}_5] = k_2[\text{NO}_2][\text{NO}_3]$$

$$[\text{NO}_2][\text{NO}_3] = \frac{k_1[\text{N}_2\text{O}_5]}{k'_1 + k_2}$$

Substituting,

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = -k_1[\text{N}_2\text{O}_5] + \frac{k'_1 k_1}{k'_1 + k_2} [\text{N}_2\text{O}_5] - \frac{k_2 k_1}{k'_1 + k_2} [\text{N}_2\text{O}_5] = -\frac{2k_1 k_2}{k'_1 + k_2} [\text{N}_2\text{O}_5]$$

$$\text{Rate} = \frac{k_1 k_2}{k'_1 + k_2} [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5]$$

**E26.6(b)**

$$\frac{d[\text{R}]}{dt} = 2k_1[\text{R}_2] - k_2[\text{R}][\text{R}_2] + k_3[\text{R}'] - 2k_4[\text{R}]^2$$

$$\frac{d[\text{R}']}{dt} = k_2[\text{R}][\text{R}_2] - k_3[\text{R}']$$

Apply the steady-state approximation to both equations

$$2k_1[\text{R}_2] - k_2[\text{R}][\text{R}_2] + k_3[\text{R}'] - 2k_4[\text{R}]^2 = 0$$

$$k_2[\text{R}][\text{R}_2] - k_3[\text{R}'] = 0$$

The second solves to  $[\text{R}'] = \frac{k_2}{k_3} [\text{R}][\text{R}_2]$

and then the first solves to  $[\text{R}] = \left( \frac{k_1}{k_4} [\text{R}_2] \right)^{1/2}$

Therefore,  $\frac{d[\text{R}_2]}{dt} = -k_1[\text{R}_2] - k_2[\text{R}_2][\text{R}] = -k_1[\text{R}_2] - k_2 \left( \frac{k_1}{k_4} \right)^{1/2} [\text{R}_2]^{3/2}$

**E26.7(b)** (a) The figure suggests that a chain-branching explosion does not occur at temperatures as low as 700 K. There may, however, be a thermal explosion regime at pressures in excess of 10<sup>6</sup> Pa.

(b) The lower limit seems to occur when

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

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

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

**E26.8(b)** The rate of production of the product is

$$\frac{d[\text{BH}^+]}{dt} = k_2[\text{HAH}^+][\text{B}]$$

$\text{HAH}^+$  is an intermediate involved in a rapid pre-equilibrium

$$\frac{[\text{HAH}^+]}{[\text{HA}][\text{H}^+]} = \frac{k_1}{k'_1} \quad \text{so} \quad [\text{HAH}^+] = \frac{k_1[\text{HA}][\text{H}^+]}{k'_1}$$

$$\text{and} \quad \frac{d[\text{BH}^+]}{dt} = \boxed{\frac{k_1 k_2}{k'_1} [\text{HA}][\text{H}^+][\text{B}]}$$

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

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

$$\text{and} \quad \frac{d[\text{BH}^+]}{dt} = \boxed{\frac{k_1 k_2 K_a^{1/2}}{k'_1} [\text{HA}]^{3/2} [\text{B}]}$$

**E26.9(b)**  $\text{A}_2$  appears in the initiation step only.

$$\frac{d[\text{A}_2]}{dt} = -k_1[\text{A}_2]$$

Consequently, the rate of consumption of  $[\text{A}_2]$  is first order in  $\text{A}_2$  and the rate is independent of intermediate concentrations.

**E26.10(b)** The maximum velocity is  $k_b[\text{E}]_0$  and the velocity in general is

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

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

**E26.11(b)** The quantum yield tells us that each mole of photons absorbed causes  $1.2 \times 10^2$  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  $1.77 \times 10^{-3} \text{ mol} / (1.2 \times 10^2 \text{ mol Einstein}^{-1}) = \boxed{1.5 \times 10^{-5} \text{ moles of photons}}$

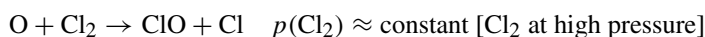
**E26.12(b)** The quantum efficiency is defined as the amount of reacting molecules  $n_A$  divided by the amount of photons absorbed  $n_{\text{abs}}$ . The fraction of photons absorbed  $f_{\text{abs}}$  is one minus the fraction transmitted  $f_{\text{trans}}$ ; and the amount of photons emitted  $n_{\text{photon}}$  can be inferred from the energy of the light source (power  $P$  times time  $t$ ) and the energy of the photons ( $hc/\lambda$ ).

$$\begin{aligned} \Phi &= \frac{n_A hc N_A}{(1 - f_{\text{trans}}) \lambda P t} \\ &= \frac{(0.324 \text{ mol}) \times (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(1 - 0.257) \times (320 \times 10^{-9} \text{ m}) \times (87.5 \text{ W}) \times (28.0 \text{ min}) \times (60 \text{ s min}^{-1})} \\ &= \boxed{1.11} \end{aligned}$$

## Solutions to problems

### Solutions to numerical problems

#### P26.2



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

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

That being so,  $\ln \frac{[\text{O}]_0}{[\text{O}]} = k't = k[\text{Cl}_2]t = k[\text{Cl}_2] \times \frac{d}{v}$

where  $k' = [\text{Cl}_2]k$ ,  $v$  is the flow rate, and  $d$  is the distance along the tube. We draw up the following table

|                                       |      |      |      |      |      |      |      |      |      |      |
|---------------------------------------|------|------|------|------|------|------|------|------|------|------|
| $d/\text{cm}$                         | 0    | 2    | 4    | 6    | 8    | 10   | 12   | 14   | 16   | 18   |
| $\ln \frac{[\text{O}]_0}{[\text{O}]}$ | 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 Fig. 26.1.

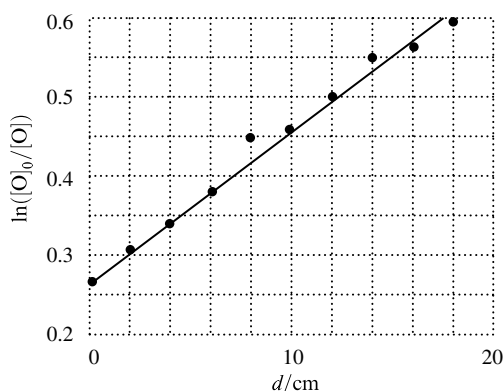


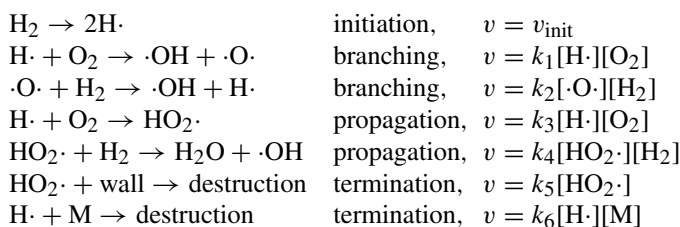
Figure 26.1

The slope is 0.0189, and so  $\frac{k[\text{Cl}_2]}{v} = 0.0189 \text{ cm}^{-1}$ .

$$\begin{aligned} \text{Therefore, } k &= \frac{(0.0189 \text{ cm}^{-1}) \times v}{[\text{Cl}_2]} \\ &= \frac{(0.0189 \text{ cm}^{-1}) \times (6.66 \times 10^2 \text{ cm s}^{-1})}{2.54 \times 10^{-7} \text{ mol L}^{-1}} = \boxed{5.0 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

(There is a very fast  $\text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2$  reaction, and so the answer given here is actually twice the true value.)

#### P26.5



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

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

Intermediates are examined with the steady-state approximation.

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

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

Therefore,

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

The factor  $(k_3[O_2] + k_6[M])$  is always positive and, therefore,  $v_{\text{rad}}$  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  $[\cdot O\cdot]$ .

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

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

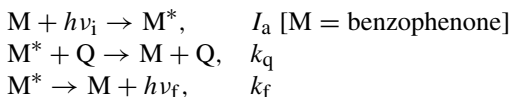
$$\begin{aligned} [H\cdot]_{\text{SS}} &= \frac{v_{\text{init}} + k_2[H_2][\cdot O\cdot]}{(k_1 + k_3)[O_2] + k_6[M]} \\ v_{\text{rad}} &= \frac{v_{\text{init}}k_1[O_2]}{(k_1 + k_3)[O_2] + k_6[M]} + \left\{ \frac{k_1k_2[H_2][O_2]}{(k_1 + k_3)[O_2] + k_6[M]} - k_2[H_2] \right\} [\cdot O\cdot] \end{aligned}$$

This has the form

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

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  $\frac{k_1[O_2]}{(k_1 + k_3)[O_2] + k_6[M]} > 1$ . 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  $H\cdot$  and  $\cdot O\cdot$ . It is, however, unlikely that the steady-state approximation can be applied to explosive reactions, and this is where the analysis breaks down.

### P26.8



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

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

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

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

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

| $10^3[Q]/M$     | 1   | 5   | 10  |
|-----------------|-----|-----|-----|
| $\frac{1}{I_f}$ | 2.4 | 4.0 | 6.3 |

The points are plotted in Fig. 26.2.

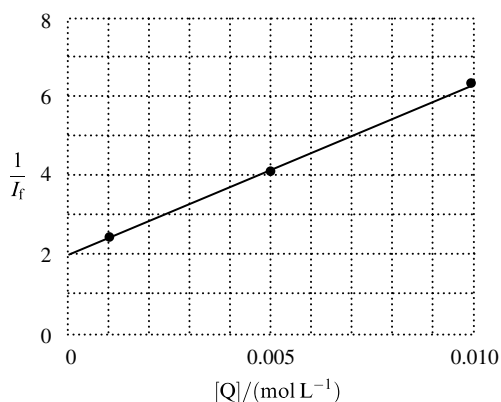


Figure 26.2

The intercept lies at 2.0, and so  $I_a = \frac{1}{2.0} = 0.50$ . The slope is 430, and so

$$\frac{k_q}{k_f I_a} = 430 \text{ L mol}^{-1}$$

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

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

### Solutions to theoretical problems

P26.11

$$\frac{d[\text{CH}_3\text{CH}_3]}{dt} = -k_a[\text{CH}_3\text{CH}_3] - k_b[\text{CH}_3][\text{CH}_3\text{CH}_3] - k_d[\text{CH}_3\text{CH}_3][\text{H}] + k_e[\text{CH}_3\text{CH}_2][\text{H}]$$

We apply the steady-state approximation to the three intermediates  $\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ , and  $\text{H}$ .

$$\frac{d[\text{CH}_3]}{dt} = 2k_a[\text{CH}_3\text{CH}_3] - k_b[\text{CH}_3\text{CH}_3][\text{CH}_3] = 0$$

which implies that  $[\text{CH}_3] = \frac{2k_a}{k_b}$ .

$$\begin{aligned} \frac{d[\text{CH}_3\text{CH}_2]}{dt} &= k_b[\text{CH}_3][\text{CH}_3\text{CH}_3] - k_c[\text{CH}_3\text{CH}_2] \\ &\quad + k_d[\text{CH}_3\text{CH}_3][\text{H}] - k_e[\text{CH}_3\text{CH}_2][\text{H}] = 0 \\ \frac{d[\text{H}]}{dt} &= k_c[\text{CH}_3\text{CH}_2] - k_d[\text{CH}_3\text{CH}_3][\text{H}] - k_e[\text{CH}_3\text{CH}_2][\text{H}] = 0 \end{aligned}$$

These three equations give

$$\begin{aligned} [\text{H}] &= \frac{k_c}{k_e + k_d \frac{[\text{CH}_3\text{CH}_3]}{[\text{CH}_3\text{CH}_2]}} \\ [\text{CH}_3\text{CH}_2]^2 - \left(\frac{k_a}{k_c}\right) [\text{CH}_3\text{CH}_3][\text{CH}_3\text{CH}_2] - \left(\frac{k_a k_d}{k_c k_e}\right) [\text{CH}_3\text{CH}_3]^2 &= 0 \end{aligned}$$

$$\text{or } [\text{CH}_3\text{CH}_2] = \left\{ \left(\frac{k_a}{2k_c}\right) + \left[ \left(\frac{k_a}{2k_c}\right)^2 + \left(\frac{k_a k_d}{k_c k_e}\right) \right]^{1/2} \right\} [\text{CH}_3\text{CH}_3]$$

which implies that

$$[\text{H}] = \frac{k_c}{k_e + \frac{k_d}{\kappa}}, \quad \kappa = \left(\frac{k_a}{2k_c}\right) + \left[ \left(\frac{k_a}{2k_c}\right)^2 + \left(\frac{k_a k_d}{k_c k_e}\right) \right]^{1/2}$$

If  $k_a$  is small in the sense that only the lowest order need be retained,

$$\begin{aligned} [\text{CH}_3\text{CH}_2] &\approx \left(\frac{k_a k_d}{k_c k_e}\right)^{1/2} [\text{CH}_3\text{CH}_3] \\ [\text{H}] &\approx \frac{k_c}{k_e + k_d \left(\frac{k_c k_e}{k_a k_d}\right)^{1/2}} \approx \left(\frac{k_a k_c}{k_d k_e}\right)^{1/2} \end{aligned}$$

The rate of production of ethene is therefore

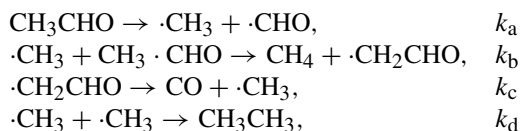
$$\frac{d[\text{CH}_2\text{CH}_2]}{dt} = k_c[\text{CH}_3\text{CH}_2] = \left(\frac{k_a k_c k_d}{k_e}\right)^{1/2} [\text{CH}_3\text{CH}_3]$$

The rate of production of ethene is equal to the rate of consumption of ethane (the intermediates all have low concentrations), so

$$\frac{d[\text{CH}_3\text{CH}_3]}{dt} = -k[\text{CH}_3\text{CH}_3], \quad k = \left(\frac{k_a k_c k_d}{k_e}\right)^{1/2}$$

Different orders may arise if the reaction is sensitized so that  $k_a$  is increased.

**P26.12**



$$\frac{d[\text{CH}_4]}{dt} = k_b[\text{CH}_3][\text{CH}_3\text{CHO}]$$

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = -k_a[\text{CH}_3\text{CHO}] - k_b[\text{CH}_3\text{CHO}][\text{CH}_3]$$



$$\frac{d[\text{CH}_3]}{dt} = k_a[\text{CH}_3\text{CHO}] - k_b[\text{CH}_3\text{CHO}][\text{CH}_3] + k_c[\text{CH}_2\text{CHO}] - 2k_d[\text{CH}_3]^2 = 0$$

$$\frac{d[\text{CH}_2\text{CHO}]}{dt} = k_b[\text{CH}_3][\text{CH}_3\text{CHO}] - k_c[\text{CH}_2\text{CHO}] = 0$$

Adding the last two equations gives

$$k_a[\text{CH}_3\text{CHO}] - 2k_d[\text{CH}_3]^2 = 0, \quad \text{or} \quad [\text{CH}_3] = \left(\frac{k_a}{2k_d}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

Therefore

$$\frac{d[\text{CH}_4]}{dt} = k_b \left(\frac{k_a}{2k_d}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} = -k_a[\text{CH}_3\text{CHO}] - k_b \left(\frac{k_a}{2k_d}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

Note that, to lowest-order in  $k_a$ ,

$$\frac{d[\text{CH}_3\text{CHO}]}{dt} \approx -k_b \left(\frac{k_a}{2k_d}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

and the reaction is three-halves order in  $\text{CH}_3\text{CHO}$ .

**P26.14** (a)  $\bar{M}_n^3 = M^3 \sum_n n^3 P_n = M^3 (1-p) \sum_n n^3 p^{n-1}$  [ $P_n = p^{n-1}(1-p)$ , Problem 26.13]

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

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

$$\bar{M}_n^2 = \frac{M^2(1+p)}{(1-p)^2} \text{ [Problem 26.13]}$$

Therefore,  $\frac{\bar{M}_n^3}{\bar{M}_n^2} = \boxed{\frac{M(1+4p+p^2)}{1-p^2}}$

(b)  $\langle n \rangle = \frac{1}{1-p}$  [26.8], so  $p = 1 - \frac{1}{\langle n \rangle}$

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

**P26.16**  $\frac{d[\text{A}]}{dt} = -k[\text{A}]^2[\text{OH}] = -k[\text{A}]^3$  because  $[\text{A}] = [\text{OH}]$ .

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

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

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

By eqn 26.8a the degree of polymerization,  $\langle n \rangle$ , is given by

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

**P26.18**

$$\frac{d[P]}{dt} = k[A][P]^2$$

$$\frac{dx}{dt} = k(A_0 - x)(P_0 + x)^2 \quad [x = P - P_0]$$

$$kt = \int_0^x \frac{dx}{(A_0 - x)(P_0 + x)^2}$$

Integrate by partial fractions (as in Problem 26.17)

$$\begin{aligned} kt &= \left( \frac{1}{A_0 + P_0} \right) \int_0^x \left\{ \left( \frac{1}{P_0 + x} \right)^2 + \left( \frac{1}{A_0 + P_0} \right) \left[ \frac{1}{P_0 + x} + \frac{1}{A_0 - x} \right] \right\} dx \\ &= \left( \frac{1}{A_0 + P_0} \right) \left\{ \left( \frac{1}{P_0} - \frac{1}{P_0 + x} \right) + \left( \frac{1}{A_0 + P_0} \right) \left[ \ln \left( \frac{P_0 + x}{P_0} \right) + \ln \left( \frac{A_0}{A_0 - x} \right) \right] \right\} \\ &= \left( \frac{1}{A_0 + P_0} \right) \left[ \left( \frac{x}{P_0(P_0 + x)} \right) + \left( \frac{1}{A_0 + P_0} \right) \ln \left( \frac{(P_0 + x)A_0}{P_0(A_0 - x)} \right) \right] \end{aligned}$$

Therefore, with  $y = \frac{x}{[A]_0}$  and  $p = \frac{P_0}{A_0}$ ,

$$A_0(A_0 + P_0)kt = \boxed{\left( \frac{y}{p(p + y)} \right) + \left( \frac{1}{1 + p} \right) \ln \left( \frac{p + y}{p(1 - y)} \right)}$$

As in Problem 26.6, the rate is maximum when

$$\begin{aligned} \frac{dv_P}{dt} &= 2k[A][P] \left( \frac{d[P]}{dt} \right) + k \left( \frac{d[A]}{dt} \right) [P]^2 \\ &= 2k[A][P]v_P - k[P]^2v_P = k[P](2[A] - [P])v_P = 0 \end{aligned}$$

That is, at  $[A] = \frac{1}{2}[P]$

On substitution of this condition into the integrated rate law, we find

$$A_0(A_0 + P_0)kt_{\max} = \left( \frac{2 - p}{2p(1 + p)} \right) + \left( \frac{1}{1 + p} \right) \ln \frac{2}{p}$$

$$\text{or } (A_0 + P_0)^2 kt_{\max} = \boxed{\frac{2 - p}{2p} + \ln \frac{2}{p}}$$

**P26.20**

$$(i) \quad \frac{d[X]}{dt} = k_a[A][Y] - k_b[X][Y] + k_c[A][X] - 2k_d[X]^2$$

$$(ii) \quad \frac{d[Y]}{dt} = -k_a[A][Y] - k_b[X][Y] - k_e[Z]$$

Express these differential equations as finite-difference equations

$$(i) \quad X(t_{i+1}) = X(t_i) + \{k_a[A]Y(t_i) - k_bX(t_i)Y(t_i) + k_c[A]X(t_i) - 2k_dX^2(t_i)\}\Delta t$$

$$(ii) \quad Y(t_{i+1}) = Y(t_i) + \{k_c[Z] - k_a[A]Y(t_i) - k_bX(t_i)Y(t_i)\}\Delta t$$

Solve these equations by iteration.

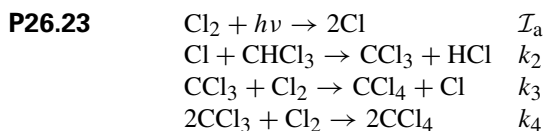
**P26.21**  $A \rightarrow B \quad \frac{d[B]}{dt} = \mathcal{I}_a$

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

In the photostationary state  $\mathcal{I}_a - k[B]^2 = 0$ . Hence,

$$[B] = \left[ \frac{\mathcal{I}_a}{k} \right]^{1/2} \propto [A]^{1/2} \quad [\text{because } \mathcal{I} \propto [A]]$$

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.



$$(i) \quad \frac{d[\text{CCl}_4]}{dt} = 2k_4[\text{CCl}_3]^2[\text{Cl}_2] + k_3[\text{CCl}_3][\text{Cl}_2]$$

$$(ii) \quad \frac{d[\text{CCl}_3]}{dt} = k_2[\text{Cl}][\text{CHCl}_3] - k_3[\text{CCl}_3][\text{Cl}_2] - 2k_4[\text{CCl}_3]^2[\text{Cl}_2] = 0$$

$$(iii) \quad \frac{d[\text{Cl}]}{dt} = 2\mathcal{I}_a - k_2[\text{Cl}][\text{CHCl}_3] + k_3[\text{CCl}_3][\text{Cl}_2] = 0$$

$$(iv) \quad \frac{d[\text{Cl}_2]}{dt} = -\mathcal{I}_a - k_3[\text{CCl}_3][\text{Cl}_2] - k_4[\text{CCl}_3]^2[\text{Cl}_2]$$

Therefore,  $\mathcal{I}_a = k_4[\text{CCl}_3]^2[\text{Cl}_2]$  [(ii) + (iii)]

which implies that

$$[\text{CCl}_3] = \left( \frac{1}{k_4} \right)^{1/2} \left( \frac{\mathcal{I}_a}{[\text{Cl}_2]} \right)^{1/2}$$

Then, with (i),

$$\frac{d[\text{CCl}_4]}{dt} = 2\mathcal{I}_a + \frac{k_3\mathcal{I}_a^{1/2}[\text{Cl}]^{1/2}}{k_4^{1/2}}$$

When the pressure of chlorine is high, and the initiation rate is slow (in the sense that the lowest powers of  $\mathcal{I}_a$  dominate), the second term dominates the first, giving

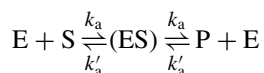
$$\frac{d[\text{CCl}_4]}{dt} = \frac{k_3\mathcal{I}_a^{1/2}}{k_4^{1/2}}[\text{Cl}_2]^{1/2} = \boxed{k\mathcal{I}_a^{1/2}[\text{Cl}_2]^{1/2}}$$

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

### Solutions to applications

#### P26.26

The mechanism considered is



We apply the steady-state approximation to [(ES)].

$$\frac{d[ES]}{dt} = k_a[E][S] - k'_a[(ES)] - k_b[(ES)] + k'_b[E][P] = 0$$

Substituting  $[E] = [E]_0 - [(ES)]$  we obtain

$$k_a([E]_0 - [(ES)])[S] - k'_a[(ES)] - k_b[(ES)] + k'_b([E]_0 - [(ES)])[P] = 0$$

$$(-k_a[S] - k'_a - k_b - k'_b[P])[(ES)] + k_a[E]_0[S] - k'_b[E]_0[P] = 0$$

$$[(ES)] = \frac{k_a[E]_0[S] + k'_b[E]_0[P]}{k_a[S] + k'_a + k_b + k'_b[P]} = \frac{[E]_0[S] + \left(\frac{k'_b}{k_a}\right)[E]_0[P]}{K_M + [S] + \left(\frac{k'_b}{k_a}\right)[P]} \quad \left[ K_M = \frac{k'_a + k_b}{k_a} \right]$$

$$\begin{aligned} \text{Then, } \frac{d[P]}{dt} &= k_b[(ES)] - k'_b[P][E] = k_b \frac{[E]_0[S] + \left(\frac{k'_b}{k_a}\right)[E]_0[P]}{K_M + [S] + \left(\frac{k'_b}{k_a}\right)[P]} - k'_b[P] \\ &\quad \times \left( [E]_0 - \frac{[E]_0[S] + \left(\frac{k'_b}{k_a}\right)[E]_0[P]}{K_M + [S] + \left(\frac{k'_b}{k_a}\right)[P]} \right) \\ &= \frac{k_b \left[ [E]_0[S] + \left(\frac{k'_b}{k_a}\right)[E]_0[P] \right] - k'_b[E]_0[P]K_M}{K_M + [S] + \left(\frac{k'_b}{k_a}\right)[P]} \end{aligned}$$

Substituting for  $K_M$  in the numerator and rearranging

$$\frac{d[P]}{dt} = \frac{k_b[E]_0[S] + \left(\frac{k'_a k'_b}{k_a}\right)[E]_0[P]}{K_M + [S] + \left(\frac{k'_b}{k_a}\right)[P]}$$

For large concentrations of substrate, such that  $[S] \gg K_M$  and  $[S] \gg [P]$ ,

$$\frac{d[P]}{dt} = k_b[E]_0$$

which is the same as the unmodified mechanism. For  $[S] \gg K_M$ , but  $[S] \approx [P]$

$$\frac{d[P]}{dt} = k_b[E]_0 \left\{ \frac{[S] - (k/k'_b)[P]}{[S] + (k/k'_a)[P]} \right\} \quad k = \frac{k'_a k'_b}{k_a}$$

$$\text{For } [S] \rightarrow 0, \quad \frac{d[P]}{dt} = \frac{-k'_a k'_b [E]_0 [P]}{k'_a + k_b + k'_b [P]} = \frac{-k'_a [E]_0 [P]}{k_P + [P]}$$

$$\text{where } k_P = \frac{k'_a + k_b}{k'_b}$$

**Comment.** The negative sign in the expression for  $\frac{d[P]}{dt}$  for the case  $[S] \rightarrow 0$  is to be interpreted to mean that the mechanism in this case is the reverse of the mechanism for the case  $[P] \rightarrow 0$ . The roles of P and S are interchanged.

**Question.** Can you demonstrate the last statement in the comment above?

**P26.28** 
$$v = \frac{v_{\max}}{1 + K_M [S]_0} \quad [26.21]$$

Taking the inverse and multiplying by  $v_{\max} v$ , we find that

$$v_{\max} = v + K_M \frac{v}{[S]_0}$$

Thus,

$$v = v_{\max} - K_M \frac{v}{[S]_0} \quad \text{or} \quad \boxed{\frac{v}{[S]_0} = \frac{v_{\max}}{K_M} - \frac{v}{K_M}}$$

The regression slope and intercept of the Eadie–Hofstee data plot of  $v$  against  $v/[S]_0$  gives  $-K_M$  and  $v_{\max}$ , respectively. Alternatively, the regression slope and intercept of an Eadie–Hofstee data plot of  $v/[S]_0$  against  $v$  gives  $-1/K_M$ , and  $v_{\max}/K_M$ , respectively. The slope and intercept of the latter plot can be used to in the calculation of  $K_M$  and  $v_{\max}$ .

**P26.32** 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

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

$$1 - T = 1 - 10^{-\{(260 \text{ L mol}^{-1} \text{ cm}^{-1}) \times (8 \times 10^{-9} \text{ mol L}^{-1}) \times (10^5 \text{ cm})\}} = 0.38$$

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

$$\begin{aligned} v &= \Phi(1 - T)F = (0.94) \times (0.38) \times \frac{(1 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}) \times (1000 \text{ cm}^3 \text{ L}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10^5 \text{ cm})} \\ &= \boxed{5.9 \times 10^{-13} \text{ mol L}^{-1} \text{ s}^{-1}} \end{aligned}$$