

CHEM 402—Physical Chemistry
Chapter 23 Homework Solutions

E23.8(a) For a source of power P and wavelength λ , the amount of photons (n_λ) generated in a time t is

$$n_\lambda = \frac{Pt}{h\nu N_A} = \frac{P\lambda t}{hcN_A} = \frac{(100 \text{ W}) \times (45) \times (60 \text{ s}) \times (490 \times 10^{-9} \text{ m})}{(6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 1.11 \text{ mol.}$$

The amount of photons absorbed is 60 per cent of this incident flux, or 0.664 mol. Therefore,

$$\phi = \frac{0.344 \text{ mol}}{0.664 \text{ mol}} = \boxed{0.518}.$$

Alternatively, expressing the amount of photons in einsteins [1 mol photons = 1 einstein], $\phi = 0.518 \text{ mol einstein}^{-1}$.

Solutions to problems

Solutions to numerical problems

P23.2 $\text{O} + \text{Cl}_2 \rightarrow \text{ClO} + \text{Cl}$ $p(\text{Cl}_2) \approx \text{constant}$ [Cl_2 at high pressure]

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/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 Figure 23.1.

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

$$\text{Therefore, } k = \frac{(0.0189 \text{ cm}^{-1}) \times v}{[\text{Cl}_2]}$$

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

(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.)

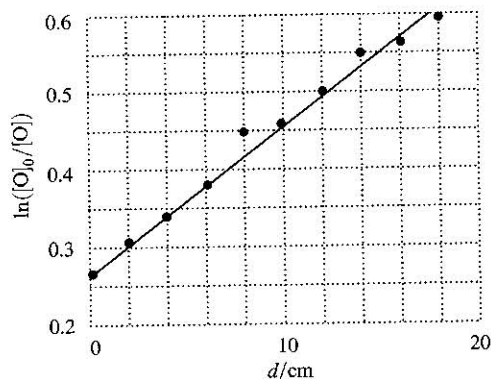
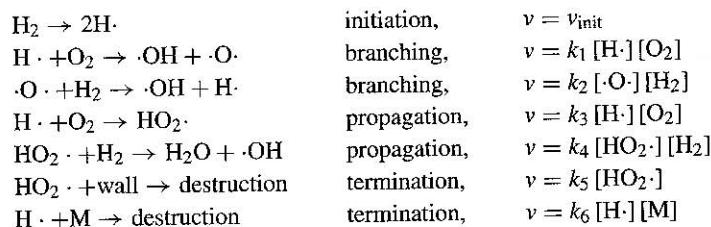


Figure 23.1

P23.4



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

$$v_{\text{rad}} = v_{\text{init}} - k_1 [\text{H}\cdot] [\text{O}_2] + k_2 [\cdot\text{O}\cdot] [\text{H}_2] - k_3 [\text{H}\cdot] [\text{O}_2] - k_6 [\text{H}\cdot] [\text{M}]$$

Intermediates are examined with the steady-state approximation.

$$\frac{d[\cdot\text{O}\cdot]}{dt} = k_1 [\text{H}\cdot] [\text{O}_2] - k_2 [\cdot\text{O}\cdot] [\text{H}_2] \approx 0$$

$$[\cdot\text{O}\cdot]_{\text{ss}} \approx \frac{k_1 [\text{H}\cdot] [\text{O}_2]}{k_2 [\text{H}_2]}$$

Therefore,

$$v_{\text{rad}} = v_{\text{init}} - k_1 [\text{H}\cdot] [\text{O}_2] + k_2 \left(\frac{k_1 [\text{H}\cdot] [\text{O}_2]}{k_2 [\text{H}_2]} \right) [\text{H}_2] - k_3 [\text{H}\cdot] [\text{O}_2] - k_6 [\text{H}\cdot] [\text{M}]$$

$$= v_{\text{init}} - (k_3 [\text{O}_2] + k_6 [\text{M}]) [\text{H}\cdot]$$

The factor $(k_3 [\text{O}_2] + k_6 [\text{M}])$ is always positive and, therefore, v_{rad} always decreases for all values of $[\text{H}\cdot]$. No explosion is possible according to this mechanism, or at least no exponential growth of $[\text{H}\cdot]$ is observed.

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

$$v_{\text{rad}} = k_1 [\text{H}\cdot] [\text{O}_2] - k_2 [\cdot\text{O}\cdot] [\text{H}_2]$$

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

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

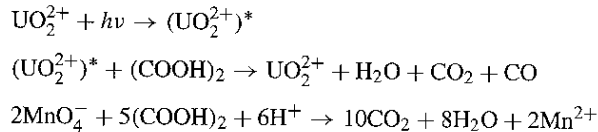
$$v_{\text{rad}} = \frac{v_{\text{init}} k_1 [O_2]}{(k_1 + k_3) [O_2] + k_6 [M]} + \left\{ \frac{k_1 k_2 [H_2] [O_2]}{(k_1 + k_3) [O_2] + k_6 [M]} - k_2 [H_2] \right\} [\cdot O\cdot]$$

This has the form

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

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 $k_1 [O_2] / ((k_1 + k_3) [O_2] + k_6 [M]) > 1$. 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 $\cdot O$. 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



17.0 cm³ of 0.212 M KMnO₄ is equivalent to

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

The initial sample contained 5.232 g (COOH)₂, corresponding to

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

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

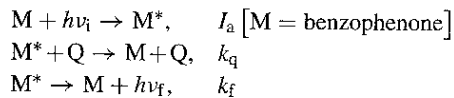
$$\frac{4.91 \times 10^{-2} \text{ mol}}{0.53} = 9.3 \times 10^{-2} \text{ mol}$$

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

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

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

P23.8



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

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

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

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

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
$1/I_f$	2.4	4.0	6.3

The points are plotted in Figure 23.2.

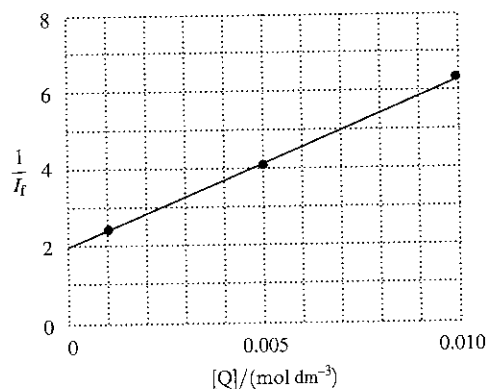


Figure 23.2

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

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

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

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

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

$$\begin{aligned}
 [\text{SiH}_3\text{O}] &= \frac{-2k_1k_6[\text{N}_2\text{O}] \pm (4k_1^2k_6^2[\text{N}_2\text{O}]^2 + 4k_1k_4k_5k_6[\text{N}_2\text{O}]^2[\text{SiH}_4])^{1/2}}{2k_5k_6[\text{SiH}_4]} \\
 &= \frac{k_1[\text{N}_2\text{O}]}{k_5[\text{SiH}_4]} \left[-1 + \left(1 + \frac{k_4k_5[\text{SiH}_4]}{k_1k_6} \right)^{1/2} \right].
 \end{aligned}$$

If k_1 is small, then

$$[\text{SiH}_3\text{O}] \approx \frac{k_1[\text{N}_2\text{O}]}{k_5[\text{SiH}_4]} \left(\frac{k_4k_5[\text{SiH}_4]}{k_1k_6} \right)^{1/2} = [\text{N}_2\text{O}] \left(\frac{k_1k_4}{k_5k_6[\text{SiH}_4]} \right)^{1/2}.$$

Putting it all together yields

$$\frac{d[\text{SiH}_4]}{dt} = -2k_1[\text{N}_2\text{O}] - k_5[\text{SiH}_4][\text{N}_2\text{O}] \left(\frac{k_1k_4}{k_5k_6[\text{SiH}_4]} \right)^{1/2} \approx \boxed{\left(\frac{k_1k_4k_5}{k_6} \right)^{1/2} [\text{N}_2\text{O}][\text{SiH}_4]^{1/2}}.$$

P23.5

$$\frac{d[\text{HI}]}{dt} = 2k_b[\text{I}\cdot]^2[\text{H}_2]. \quad (1)$$

$$\frac{d[\text{I}\cdot]}{dt} = 2k_a[\text{I}_2] - 2k'_a[\text{I}\cdot]^2 - 2k_b[\text{I}\cdot]^2[\text{H}_2].$$

In the steady-state approximation for $[\text{I}\cdot]$,

$$\frac{d[\text{I}\cdot]}{dt} = 0 = 2k_a[\text{I}_2] - 2k'_a[\text{I}\cdot]_{\text{SS}}^2 - 2k_b[\text{I}\cdot]_{\text{SS}}^2[\text{H}_2]$$

$$[\text{I}\cdot]_{\text{SS}}^2 = \frac{k_a}{k'_a + k_b[\text{H}_2]}[\text{I}_2]. \quad (2)$$

Substitution of (2) into (1) gives

$$\frac{d[\text{HI}]}{dt} = \frac{2k_b k_a [\text{I}_2][\text{H}_2]}{k'_a + k_b[\text{H}_2]}.$$

This simple rate law is observed when step (b) is rate-determining so that step (a) is a rapid equilibrium and $[\text{I}\cdot]$ is in an approximate steady state. This is equivalent to $k_b[\text{H}_2] \ll k'_a$ and hence,

$$\frac{d[\text{HI}]}{dt} = 2k_b K [\text{I}_2][\text{H}_2]$$

P23.7

$$(a) \frac{I_f}{I_0} = e^{-t/\tau_0} \quad [23.31] \quad \text{or} \quad \ln\left(\frac{I_f}{I_0}\right) = -\frac{t}{\tau_0}.$$

A plot of $\ln(I_f/I_0)$ against t should be linear with a slope equal to $-1/\tau_0$ (i.e. $\tau_0 = -1/\text{slope}$) and an intercept equal to zero. Consequently, we make the plot to determine whether it is linear. If it is linear (it is), we do a linear regression fit with a zero intercept and use the regression slope to calculate τ_0 . See Fig. 23.2. Alternatively, average the experimental values of $(1/t) \ln(I_f/I_0)$ and check that the standard deviation is a small fraction of the average (it is). The average equals $-1/\tau_0$ (i.e. $\tau_0 = -1/\text{average}$).

$$\text{Slope} = -0.150 \text{ ns}^{-1},$$

$$\tau_0 = -(-0.150 \text{ ns}^{-1})^{-1},$$

$$\tau_0 = 6.67 \text{ ns}.$$

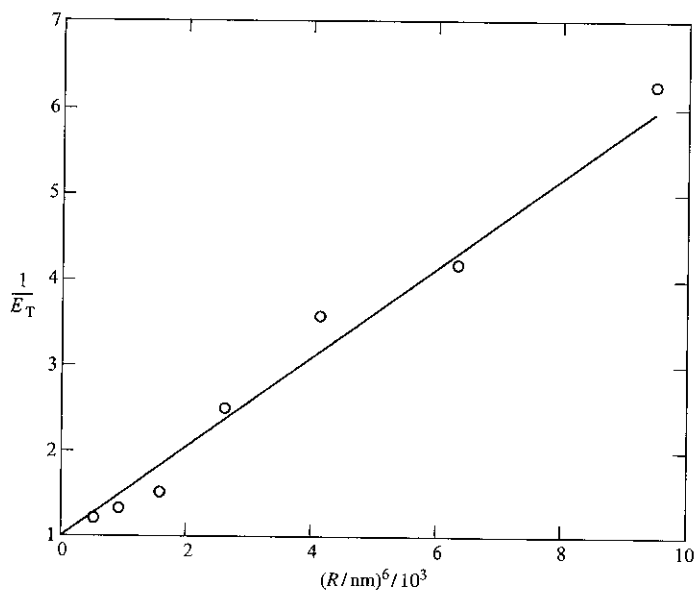
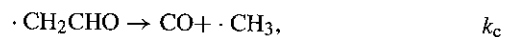
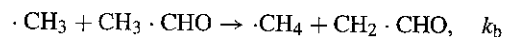


Figure 23.3

two data points at lowest R must be excluded from the mean as they are highly uncertain. $R_0 = 3.52 \text{ nm}$ with a standard deviation of 0.173 nm .

Solutions to theoretical problems

P23.12



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

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

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

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

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 CH_3CHO .

P23.14 (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 23.13]

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

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

$$\bar{M}_n^2 = \frac{M^2 (1+p)}{(1-p)^2} \text{ [Problem 23.13]}$$

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

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

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

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

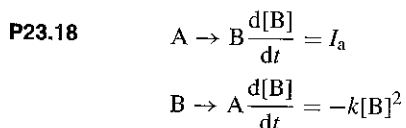
$$\frac{d[\text{A}]}{[\text{A}]^3} = -k dt \quad \text{and} \quad \int_{[\text{A}]_0}^{[\text{A}]} \frac{d[\text{A}]}{[\text{A}]^3} = -k \int_0^t dt = -kt$$

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

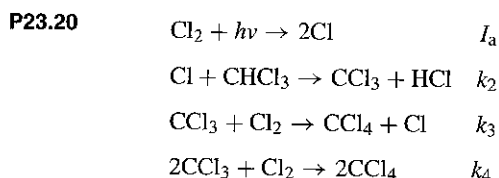
$$\langle n \rangle = \frac{[\text{A}]_0}{[\text{A}]} = \frac{1}{(1 + 2kt[\text{A}]_0)^{1/2}}$$



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

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

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.



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

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

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

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

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

which implies that

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

Then, with (i),

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

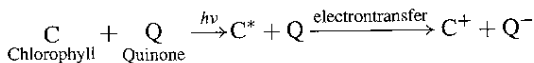
When the pressure of chlorine is high, and the initiation rate is slow (in the sense that the lowest powers of I_a dominate), the second term dominates the first, giving

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

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

$$\frac{a}{r} > S_0 \quad [\text{infection dies out}]$$

P23.30



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:

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

where U_{LUMO} and U_{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

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

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

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

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

P23.34

The rate of reaction for this reaction is

$$v = k[\text{Cl}][\text{O}_3]$$

$$\begin{aligned} \text{(a)} \quad v &= (1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \exp(-260 \text{ K}/220 \text{ K}) \times (5 \times 10^{-17} \text{ mol dm}^{-3}) \\ &\quad \times (8 \times 10^{-9} \text{ mol dm}^{-3}) \\ &= \boxed{2.1 \times 10^{-15} \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad v &= (1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) \exp(-260 \text{ K}/270 \text{ K}) \times (3 \times 10^{-15} \text{ mol dm}^{-3}) \\ &\quad \times (8 \times 10^{-11} \text{ mol dm}^{-3}) \\ &= \boxed{1.6 \times 10^{-15} \text{ mol dm}^{-3} \text{ s}^{-1}} \end{aligned}$$