

CHEM 402—Physical Chemistry
Chapter 22 Homework Solutions

Express the C–H vibrational wavenumber in terms of its force constant:

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{k_f}{\mu_{\text{CH}}} \right)^{1/2} \quad \text{so} \quad \lambda = \left(\frac{\hbar k_f^{1/2}}{2k_{\text{B}}T} \right) \times \left(\frac{1}{\mu_{\text{CH}}^{1/2}} - \frac{1}{\mu_{\text{CD}}^{1/2}} \right).$$

Compute $\frac{k(\text{C-D})}{k(\text{C-H})}$ and see if this accounts for the difference.

$$\mu_{\text{CD}} \approx \frac{2 \times 12}{2 + 12} \text{u} = 1.71 \text{u} \quad \text{and} \quad \mu_{\text{CH}} \approx \frac{1 \times 12}{1 + 12} \text{u} = 0.92 \text{u}.$$

$$\begin{aligned} \lambda &\approx \left(\frac{(1.054 \times 10^{-34} \text{J s}) \times (450 \text{N m}^{-1})^{1/2}}{(2) \times (1.381 \times 10^{-23} \text{J K}^{-1}) \times (298 \text{K})} \right) \\ &\quad \times \left(\frac{1}{(0.92 \text{u})^{1/2}} - \frac{1}{(1.71 \text{u})^{1/2}} \right) \times \left(\frac{1 \text{u}}{1.66 \times 10^{-27} \text{kg}} \right)^{1/2} \\ &\approx 1.85. \end{aligned}$$

Hence, $\frac{k(\text{C-D})}{k(\text{C-H})} = e^{-1.85} = \boxed{0.156}$.

That is, $k(\text{C-H}) \approx 6.4 \times k(\text{C-D})$, in reasonable accord with the data.

E22.16(a) $\frac{1}{k} = \frac{k'_a}{k_a k_b} + \frac{1}{k_a p_A}$ [analogous to 22.67].

Therefore, for two different pressures we have

$$\frac{1}{k} - \frac{1}{k'} = \frac{1}{k_a} \left(\frac{1}{p} - \frac{1}{p'} \right)$$

$$\begin{aligned} \text{and hence } k_a &= \frac{(1/p) - (1/p')}{((1/k) - (1/k'))} = \frac{\left(\frac{1}{12 \text{Pa}} - \frac{1}{1.30 \times 10^3 \text{Pa}} \right)}{\left(\frac{1}{2.10 \times 10^{-5} \text{s}^{-1}} - \frac{1}{2.50 \times 10^{-4} \text{s}^{-1}} \right)} \\ &= 1.9 \times 10^{-6} \text{Pa}^{-1} \text{s}^{-1}, \end{aligned}$$

or $\boxed{1.9 \text{MPa}^{-1} \text{s}^{-1}}$.

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:

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

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 ($A = (\text{CH}_3)_3\text{CBr}$)

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

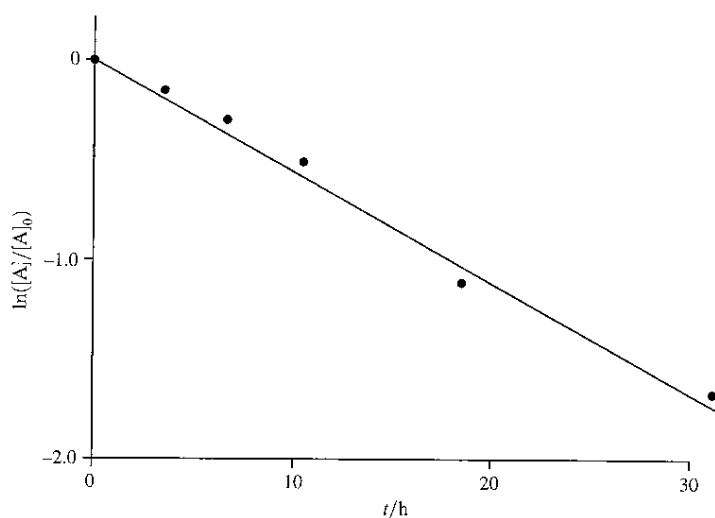


Figure 22.1

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 **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:

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

At 43.8 h

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

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

P22.4

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

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad [22.12b, A = \text{N}_2\text{O}_5]$$

Solving for k ,

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

At $t = 1.00$ min, $[A] = 0.705$ mol dm⁻³ and

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

At $t = 3.00$ min, $[A] = 0.399$ mol dm⁻³ and

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

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

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

P22.6

Since both reactions are first-order, we have

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

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

We are interested in the yield of ketene, CH₂CO; 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

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

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

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

which works out in this case to be independent of time

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

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:

$$[\text{A}] = [\text{A}]_0 - 2[\text{B}]$$

When the reaction goes to completion, $[\text{B}] = [\text{A}]_0/2$; hence $[\text{A}]_0 = 0.624 \text{ mol dm}^{-3}$. We can therefore tabulate $[\text{A}]$, 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

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

which follows from

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

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

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

$$\nu = -\frac{1}{2} \frac{d[\text{A}]}{dt} = -\left(\frac{1}{2}\right) \times (-k_{\text{A}}[\text{A}]) = \frac{1}{2} k_{\text{A}}[\text{A}]$$

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

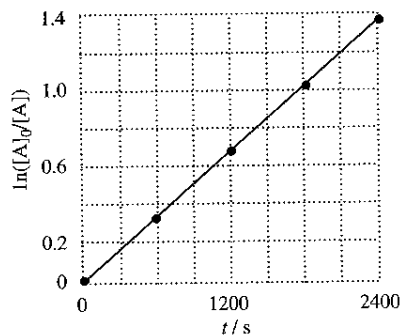


Figure 22.2

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

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

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 |
| $10^4 \left(\frac{1}{t/\text{s}}\right) \ln\frac{p_0}{p}$ | 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 **first-order kinetics** with $k = 7.2 \times 10^{-4} \text{ s}^{-1}$

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 $k_2 = 1 \text{ s}^{-1}$ for all curves and k_1 varies. The thickest curve, labeled 10, corresponds to $k_2 = 10 \text{ s}^{-1}$, as specified in part a of the problem. As the ratio k_1/k_2 gets smaller (or, as the problem puts it, the ratio k_2/k_1 gets larger), the concentration profile for I becomes lower, broader, and flatter; that is, [I] becomes more nearly constant over a longer period of time. This is the nature of the **steady-state approximation**, which becomes more and more valid as consumption of the intermediate becomes fast compared with its formation.

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

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

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.

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 |
| $10^{-7} k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | 1.44 | 1.44 | 3.03 |
| $10^{-7} k'/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | 3.03 | 6.9 | 6.9 |
| $E_a/(\text{kJ mol}^{-1})$ | 15.5 | 16.7 | 18.0 |

The mean is 16.7 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 |
| $10^{-7} k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | 1.44 | 3.03 | 6.9 |
| E_a/RT | 6.69 | 5.89 | 5.12 |
| $10^{-10} A/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ | 1.16 | 1.10 | 1.16 |

The mean is $1.14 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

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

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

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

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

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

$$\text{so } \Delta_r S^\ominus = R \ln\left(\frac{A}{A'}\right) = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{1.0 \times 10^9}{1.4 \times 10^{11}}\right) = -41.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\text{C}_2\text{H}_6) + \Delta_f H^\ominus(\text{Br}) - \Delta_f H^\ominus(\text{C}_2\text{H}_5) - \Delta_f H^\ominus(\text{HBr})$$

$$\text{so } \Delta_f H^\ominus(\text{C}_2\text{H}_5) = \Delta_f H^\ominus(\text{C}_2\text{H}_6) + \Delta_f H^\ominus(\text{Br}) - \Delta_f H^\ominus(\text{HBr}) - \Delta_r H^\ominus$$

$$\text{and } \Delta_f H^\ominus(\text{C}_2\text{H}_5) = [(-84.68) + 111.88 - (-36.40) - (-57.5)] \text{ kJ mol}^{-1} = \boxed{121.2 \text{ kJ mol}^{-1}}$$

Similarly

$$S_m^\ominus(\text{C}_2\text{H}_5) = [229.60 + 175.02 - 198.70 - (-41.1)] \text{ J mol}^{-1} \text{ K}^{-1} = \boxed{247.0 \text{ J K}^{-1} \text{ mol}^{-1}}$$

Finally

$$\begin{aligned} \Delta_f G^\ominus(\text{C}_2\text{H}_5) &= [-32.82 + 82.396 - (-53.45)] \text{ kJ mol}^{-1} - \Delta_r G^\ominus \\ &= 103.03 \text{ kJ mol}^{-1} - \Delta_r G^\ominus \end{aligned}$$

but

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_r H^\ominus - T \Delta_r S^\ominus = -57.5 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-41.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= -45.3 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{so } \Delta_f G^\ominus(\text{C}_2\text{H}_5) = [103.03 - (-45.3)] \text{ kJ mol}^{-1} = \boxed{148.3 \text{ kJ mol}^{-1}}$$

Solutions to theoretical problems

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

$$K = \frac{[\text{A}]^2}{[\text{A}_2]}, \quad \text{implying that } [\text{A}] = K^{1/2}[\text{A}_2]^{1/2}$$

The rate-determining step then gives

$$v = \frac{d[\text{P}]}{dt} = k_2[\text{A}][\text{B}] = \boxed{k_2 K^{1/2}[\text{A}_2]^{1/2}[\text{B}]} = k_{\text{eff}}[\text{A}_2]^{1/2}[\text{B}]$$

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

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

Let the initial concentrations be $[\text{A}]_0 = A_0$, $[\text{B}]_0 = B_0$, and $[\text{P}]_0 = 0$. 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

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

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 steady-state intermediate.

P22.26 Let the forward rates be written as

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

and the reverse rates as

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

The net rates are then

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

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

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

From the second of these equations we find

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

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

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

which yields, upon isolating $[B]$,

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

Thus, at the steady state

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

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,

$$\frac{d[B]}{dt} = k_1[A]_0 - (k'_1 + k_2)[B] + k'_2[C] \approx 0$$

$$\text{and } \frac{d[C]}{dt} = k_2[B] - (k'_2 + k_3)[C] \approx 0$$

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