

Thermodynamics: Examples for chapter 9.

1. N-bromoacetanilide (A) reacts to 4-bromoacetanilide (B) in dichloromethane at 15 ° according to the following kinetics:

t (hr)	0	4.0	10.5	23.0	31.5	45.0	48.0
$10^2 \times [A]$ (M)	1.00	0.907	0.762	0.566	0.466	0.348	0.321

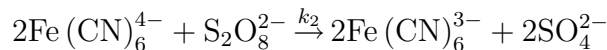
Determine the first-order rate constant, k_1 , and the half-life $t_{1/2}$.

Solution:

Approximately halfway between 23.0 hr and 31.5 hr $[A] \approx 0.5$. Thus the half-life is 27.3 hr or about 10^5 s. More accurate results could be obtained by fitting the integrated form of the 1st order rate equation to the kinetic data. The relation between $t_{1/2}$ and k_1 is:

$$k_1 = \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{10^5 \text{ s}} \approx 7 \times 10^{-6} \text{ s}^{-1}$$

2. The oxidation of $\text{Fe}(\text{CN})_6^{4-}$ to $\text{Fe}(\text{CN})_6^{3-}$ by peroxodisulfate, $\text{S}_2\text{O}_8^{2-}$, can be monitored spectrophotometrically by observing the increase in absorbance at 420 nm, $A_{420 \text{ nm}}$:



with the differential rate-law:

$$-\frac{1}{2} \frac{d[\text{Fe}(\text{CN})_6^{4-}]}{dt} = k_2 [\text{Fe}(\text{CN})_6^{4-}] [\text{S}_2\text{O}_8^{2-}]$$

Under the pseudo-first-order conditions with $[\text{S}_2\text{O}_8^{2-}] = 1.8 \times 10^{-2} \text{ M}$ and $[\text{Fe}(\text{CN})_6^{4-}] = 6.5 \times 10^{-4} \text{ M}$, the following absorbances were recorded at 25 °C:

t (s)	0	900	1800	2700	3600	4500	∞
$A_{420 \text{ nm}}$	0.120	0.290	0.420	0.510	0.581	0.632	0.781

Calculate the pseudo-first-order rate constant, $k_1 = k_2 [\text{S}_2\text{O}_8^{2-}]$, and then the second-order rate constant k_2 .

Solution:

According to the Lambert-Beer law, $A_{420 \text{ nm}} \propto [\text{Fe}(\text{CN})_6^{3-}]$. The rate of $\text{Fe}(\text{CN})_6^{3-}$ disappearance and $\text{Fe}(\text{CN})_6^{4-}$ appearance have the same magnitude but opposite sign:

$$-\frac{1}{2} \frac{d [\text{Fe}(\text{CN})_6^{4-}]}{dt} = \frac{1}{2} \frac{d [\text{Fe}(\text{CN})_6^{3-}]}{dt}$$

and also $[\text{Fe}(\text{CN})_6^{3-}] = [\text{Fe}(\text{CN})_6^{4-}]_0 - [\text{Fe}(\text{CN})_6^{4-}]$.

The above two relations can be combined as:

$$\frac{1}{2} \frac{d [\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_2 ([\text{Fe}(\text{CN})_6^{4-}]_0 - [\text{Fe}(\text{CN})_6^{3-}]) \times [\text{S}_2\text{O}_8^{2-}]$$

Since perxodisulfide is in excess, its concentration is approximately constant and we can treat the system as pseudo-first-order reaction:

$$\frac{1}{2} \frac{d [\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_1 ([\text{Fe}(\text{CN})_6^{4-}]_0 - [\text{Fe}(\text{CN})_6^{3-}])$$

The solution to this differential equation is:

$$[\text{Fe}(\text{CN})_6^{3-}] = [\text{Fe}(\text{CN})_6^{4-}]_0 \times (1 - e^{-2k_1 t})$$

Since $A_{420 \text{ nm}} \propto [\text{Fe}(\text{CN})_6^{3-}]$, we proceed in fitting:

$$A_{420 \text{ nm}} = C \times (1 - e^{-2k_1 t})$$

Before fitting the data, one should notice that there is a baseline absorption at 420 nm since $A \neq 0$ at $t = 0$ (see the table of experimental data given). So first subtract 0.120 off from all the given values. Least squares fit to the above equation then yields $k_1 = 1.7 \times 10^{-4} \text{ s}^{-1}$ and further $k_2 = \frac{k_1}{[\text{S}_2\text{O}_8^{2-}]} = \frac{1.7 \times 10^{-4} \text{ s}^{-1}}{1.8 \times 10^{-2} \text{ M}} = 9.4 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$.

3. First-order rate constants, k , for the rotation about the C–N bond in N,N-dimethylnicotinamide measured at different temperatures by NMR are:

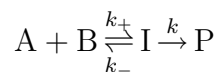
T (K)	10.0	15.7	21.5	27.5	33.2	38.5	45.7
k (s^{-1})	2.08	4.57	8.24	15.8	28.4	46.1	93.5

Determine the Arrhenius activation energy E_a and the pre-exponential factor A .

Solution:

Enter the data into qtiplot and fit the Arrhenius law to it, $k = Ae^{-E_a/(RT)}$. Remember to use K units for temperature. Least squares fitting gives $A = 6.8 \times 10^{14}$ and $E_a = 78.5$ kJ/mol.

4. Derive the expression for the product (P) concentration in the following reaction:



by using the approximation $k_- \gg k$.

Solution:

In the lecture notes it was shown that: $\frac{d[P]}{dt} = k' [A] [B]$ where $k' = \frac{k_+ k}{k_-}$. This is effectively a second-order rate equation, which can be written in integrated form as:

$$k't = \frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[A]_0 ([B]_0 - x)}{([A]_0 - x) [B]_0} \right)$$

where $[A] = [A]_0 - x$, $[B] = [B]_0 - x$, and $[P] = x$.

This can be solved for x (which is equal to $[P]$):

$$[P] = x = \frac{[B]_0 - [B]_0 e^{k't([B]_0 - [A]_0)}}{1 - \frac{[B]_0}{[A]_0} e^{k't([B]_0 - [A]_0)}}$$

5. Carry out the same calculation as in the above problem but by using the steady-state approximation.

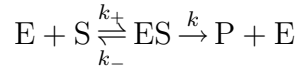
Solution:

The kinetic equations can be written as:

$$\begin{aligned}
\frac{d[P]}{dt} &= k[I] \\
\frac{d[I]}{dt} &= k_+[A][B] - k_-[I] - k[I] \approx 0 \\
\Rightarrow [I] &\approx \frac{k_+[A][B]}{k_-k} \\
\Rightarrow \frac{d[P]}{dt} &= k[I] = \frac{kk_+}{k_-+k} [A][B]
\end{aligned}$$

This is the same form as in the previous problem. The result would be the same with the exception of the value of $k' = \frac{kk_+}{k_-+k}$.

6. Show that the results of the previous problems can be used to derive the Michaelis-Menten enzyme kinetics model:



(E = enzyme, S = substrate, and P = product) with $\frac{d[P]}{dt} = k'[E]_0$, $k' = k[S]/(K_M + [S])$ and $K_M = (k_- + k_+)/k_+$. Note that the substrate is in excess compared to the enzyme and the concentration of the enzyme is conserved in the reaction.

Solution:

The previous problem gives directly:

$$[ES] = \frac{k_+[E][S]}{k_-+k}$$

Since the enzyme concentration is conserved, we have $[E] + [ES] = [E]_0$. Furthermore S is not greatly affected due to its high concentration and then $[S] \approx \text{constant}$. This gives:

$$[ES] = \frac{k_+([E]_0 - [ES])[S]}{k_-+k}$$

$$\Rightarrow [\text{ES}] = \frac{k_+ [\text{E}]_0 [\text{S}]}{k_- + k + k_+ [\text{S}]}$$

Inserting this into $\frac{d[\text{P}]}{dt} = k [\text{ES}]$ yields:

$$\frac{[\text{P}]}{dt} = \frac{k k_+ [\text{E}]_0 [\text{S}]}{k_- + k + k_+ [\text{S}]} = k' [\text{E}]$$

where $k' = \frac{k[\text{S}]}{k_M + [\text{S}]}$ and $k_M = \frac{k_- + k}{k_+}$ (Michaelis constant).
