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-rder rate constat, k_1, and the half-life $t_{1/2}$.

   Solution:

   Approximately halfway between 23.0 hr and 31.5 hr [A] ≈ 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:

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

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2. The oxidation of $\mathrm{Fe(CN)_6^{4-}}$ to $\mathrm{Fe(CN)_6^{3-}}$ by perxodisulfide, $\mathrm{S_2O_8^{2-}}$, can be monitored spectrophotometrically by observing the increase in absorbance at 420 nm, $\mathrm{A_{420\ nm}}$:

   $$2\mathrm{Fe\,(CN)_6^{4-}} + \mathrm{S_2O_8^{2-}} \xrightarrow{k_2} 2\mathrm{Fe\,(CN)_6^{3-}} + 2\mathrm{SO_4^{2-}}$$

   with the differential rate-law:

   $$-\frac{1}{2}\frac{d\left[\mathrm{Fe\,(CN)_6^{4-}}\right]}{dt} = k_2 \left[\mathrm{Fe\,(CN)_6^{4-}}\right]\left[\mathrm{S_2O_8^{2-}}\right]$$

   Under the pseudo-first-order conditions with $\left[\mathrm{S_2O_8^{-2}}\right] = 1.8 \times 10^{-2}$ M and $\left[\mathrm{Fe\,(CN)_6^{4-}}\right] = 6.5 \times 10^{-4}$ M., the following absorbances were recorded at 25 °C:

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

   Calculate the pseudo-first-order rate constant, $k_1 = k_2\left[\mathrm{S_2O_8^{2-}}\right]$, and then the second-order rate constant k_2.

   Solution:

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

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

and also $\left[\mathrm{Fe\,(CN)_6^{3-}}\right] = \left[\mathrm{Fe\,(CN)_6^{4-}}\right]_0 - \left[\mathrm{Fe\,(CN)_6^{4-}}\right]$.
The above two relations can be combined as:

$$\frac{1}{2}\frac{d\left[\mathrm{Fe\,(CN)_6^{3-}}\right]}{dt} = k_2\left(\left[\mathrm{Fe\,(CN)_6^{4-}}\right]_0 - \left[\mathrm{Fe\,(CN)_6^{3-}}\right]\right) \times \left[\mathrm{S_2O_8^{2-}}\right]$$

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

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

The solution to this differential equation is:

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

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

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

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 $k_1 = 1.7 \times 10^{-4}\ \mathrm{s^{-1}}$ and further $k_2 = \frac{k_1}{\left[\mathrm{S_2O_8^{2-}}\right]} = \frac{1.7\times10^{4}\ \mathrm{s^{-1}}}{1.8\times10^{-2}\ \mathrm{M}} = 9.4 \times 10^{-4}\ \mathrm{s^{-1}\ M^{-1}}$.

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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 ($\mathrm{s^{-1}}$)	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:

$$\mathrm{A} + \mathrm{B} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{I} \xrightarrow{k} \mathrm{P}$$

by using the approximation $k_- >> k$.

Solution:

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

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

where $[\mathrm{A}] = [\mathrm{A}]_0 - x$, $[\mathrm{B}] = [\mathrm{B}]_0 - x$, and $[\mathrm{P}] = x$.

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

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

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:

$$\frac{d\,[\mathrm{P}]}{dt} = k\,[\mathrm{I}]$$

$$\frac{d\,[\mathrm{I}]}{dt} = k_+\,[\mathrm{A}]\,[\mathrm{B}] - k_-\,[\mathrm{I}] - k\,[\mathrm{I}] \approx 0$$

$$\Rightarrow [\mathrm{I}] \approx \frac{k_+\,[\mathrm{A}]\,[\mathrm{B}]}{k_- k}$$

$$\Rightarrow \frac{d\,[\mathrm{P}]}{dt} = k\,[\mathrm{I}] = \frac{k k_+}{k_- + k}\,[\mathrm{A}]\,[\mathrm{B}]$$

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

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

$$\mathrm{E} + \mathrm{S} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{ES} \xrightarrow{k} \mathrm{P} + \mathrm{E}$$

(E = enzyme, S = substrate, and P = product) with $\frac{d[\mathrm{P}]}{dt} = k'\,[\mathrm{E}]_0$, $k' = k\,[\mathrm{S}]\,/(K_M + [\mathrm{S}])$ 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:

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

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

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

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

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

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

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