First exam: Chemical Kinetics (Chapter 13 only!)

- rates of chemical rxn
- integrated rate laws
- zero-, first, and second order rxns
- mechanisms
- rate expression <-> mechanism (fast equilibrium, steady state apprx)
- Michaelis-Menten kinetics

- T-dependence of rxn rates, Arrhenius law
- activated complex and activation energy
- catalysis
In a first-order reaction, 38.5% of the reactants have been converted to products in 480 s.

(a) Calculate the rate constant.
If the rxn is 38.5% complete, then 38.5% of the original concentration is consumed, leaving 61.5%.
Thus, \([A] = 61.5\% \text{ of } [A]_0\) or \([A] = 0.615[A]_0\).

\[
\ln\left(\frac{[A]}{[A]_0}\right) = -kt \quad \Rightarrow \quad \ln\left(\frac{0.615 [A]_0}{[A]_0}\right) = -k \cdot 480s \quad \Rightarrow \quad \ln 0.615 = -0.486 = -k \cdot 480s
\]

\[k = 1.01 \cdot 10^{-3} \text{ s}^{-1}\]

(b) What is the value of the half life?

\[
t_{\frac{1}{2}} = \ln 2 / k = 0.693 / 1.01 \cdot 10^{-3} \text{ s}^{-1} = 686s
\]

(c) How long will it take for the reaction to go to 95% completion?
\([A] = 0.05[A]_0\).

\[
\ln 0.05 = -kt = -1.01 \cdot 10^{-3} \cdot t \quad \Rightarrow \quad t = 3 \cdot 10^{3} \text{ s}
\]
Iron(II) ion is oxidized by chlorine in aqueous solution, the overall equation being

$$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$$

It is found experimentally that the rate of the overall reaction is decreased when either the Iron(III) ion or the chloride-ion concentration is increased. Two possible mechanisms can lead to this overall reaction. Write the detailed rate law that corresponds to each of them. Which of the following possible mechanisms is consistent with the experimental observations?

(a) (1) \(Fe^{2+} + Cl_2 \leftrightarrow Fe^{3+} + Cl^- + Cl\) \(k_1, k_{-1}\) (rapid equilibrium)

2) \(Fe^{2+} + Cl^- \rightarrow Fe^{3+} + Cl^-\) \(k_2\) (slow)

\[
R = \frac{d[Fe^{3+}]}{dt} = k_2[Fe^{2+}][Cl] \\
[Cl] = \frac{k_1[Fe^{2+}][Cl_2]}{k_{-1}[Fe^{3+}][Cl^-]} \\
R = \frac{k_1k_2}{k_{-1}} \cdot \frac{[Fe^{2+}]^2[Cl_2]}{[Fe^{3+}][Cl^-]} 
\]

(b) (3) \(Fe^{2+} + Cl_2 \leftrightarrow Fe^{4+} + 2Cl^-\) \(k_3, k_{-3}\) (rapid equilibrium)

(4) \(Fe^{4+} + Fe^{2+} \rightarrow 2Fe^{3+}\) \(k_4\) (slow)

\[
R = \frac{1}{2} \frac{d[Fe^{3+}]}{dt} = k_4[Fe^{4+}][Fe^{2+}] \\
[Fe^{4+}] = \frac{k_3[Fe^{2+}][Cl_2]}{k_{-3}[Cl^-]^2} \\
R = \frac{k_3k_4}{k_{-3}} \cdot \frac{[Fe^{2+}]^2[Cl_2]}{[Cl^-]^2} 
\]

Only in (a) the rate decreases with the increase of both \([Cl^-]\) and \([Fe^{3+}]\)
The rate of the reaction

$$\text{Ce}^{4+}(aq) + \text{Fe}^{2+}(aq) \rightarrow \text{Ce}^{3+}(aq) + \text{Fe}^{3+}(aq)$$

is first order in both $\text{Fe}^{2+}(aq)$ and $\text{Ce}^{4+}(aq)$ concentrations, and the rate constant $k$ is $3.7 \times 10^9$ L mol$^{-1}$ s$^{-1}$. Suppose that the initial concentration of each reactant is $c_0 = 1.0 \times 10^{-3}$ mol L$^{-1}$. Calculate the time (in seconds) required for the $\text{Ce}^{4+}(aq)$ to decrease to a concentration of $1.0 \times 10^{-4}$ mol L$^{-1}$.

$$-\frac{d[\text{Ce}^{4+}]}{dt} = k[\text{Ce}^{4+}][\text{Fe}^{2+}] \quad [\text{Ce}^{4+}] = [\text{Fe}^{2+}] \equiv c$$

$$-\frac{dc}{dt} = kc^2 \quad \frac{1}{c} = kt + \frac{1}{c_0}$$

$$t = \frac{1}{k} \left( \frac{1}{c} - \frac{1}{c_0} \right) = \frac{1}{3.7 \times 10^9} \left( \frac{1}{10^{-4}} - \frac{1}{10^{-3}} \right) = \frac{10^4 - 10^3}{3.7 \times 10^9} \frac{L \cdot \text{mol} \cdot \text{s}}{\text{mol} \cdot \text{s}} = 2.4 \times 10^{-6} \text{s}$$
The destruction of NO$_3$ in the stratosphere can be described by the following mechan

\[
\begin{align*}
\text{NO}_3 + \text{light} & \rightarrow \text{NO}_2 + \text{O} \quad k_1 \\
\text{NO}_2 + \text{O} + \text{M} & \rightarrow \text{NO}_3 + \text{M} \quad k_2 \\
\text{NO}_3 + \text{O} & \rightarrow \text{NO}_2 + \text{O}_2 \quad k_3
\end{align*}
\]

The rate constant \( k_1 \) depends on the light intensity and the wavelength.

(a) By making the steady state approximation for the concentration of the oxygen atoms (taking into account its formation and consumption in all the steps), express the rate of formation of O$_2$ in terms of the NO$_2$, NO$_3$ and M concentrations and rate constants for the elementary reactions.

\[
\begin{align*}
\frac{d[O]}{dt} &= k_1[\text{NO}_3] - k_2[O][\text{NO}_2][\text{M}] - k_3[\text{NO}_3][O] = k_1[\text{NO}_3] - (k_2[\text{NO}_2][\text{M}] + k_3[\text{NO}_3])[O] \\
\frac{d[O]}{dt} &\approx 0 \\
[O] &= \frac{k_1[\text{NO}_3]}{k_2[\text{NO}_2][\text{M}] + k_3[\text{NO}_3]} \\
R &= \frac{d[O_2]}{dt} = k_3[\text{NO}_3][O] = \frac{k_3k_1[\text{NO}_3]^2}{k_2[\text{NO}_2][\text{M}] + k_3[\text{NO}_3]}
\end{align*}
\]

(b) Determine the conditions and the ratios of rate constants that are needed for this reaction to follow first-order kinetics.

\[
R = \frac{k_1[\text{NO}_3]^2}{k_2[\text{NO}_2][\text{M}] + [\text{NO}_3]} \\
\text{When } k_2 \ll k_3 \text{ and } [\text{NO}_2] \text{ and } [\text{M}] \text{ are small, then:} \\
R \approx \frac{k_1[\text{NO}_3]^2}{[\text{NO}_3]} = k_1[\text{NO}_3]
\]
Consider the overall reaction

\[
\text{ClO}_3^- (aq) + 5\text{Cl}^- (aq) + 6\text{H}^+ (aq) \rightarrow 3\text{Cl}_2(l) + 3\text{H}_2\text{O}(l)
\]

The rate law is given by: \( R = k[\text{ClO}_3^-][\text{Cl}^-]^2[\text{H}^+] \).

The reaction was carried out under the concentration conditions

\[ [\text{ClO}_3^-]_0 = 1.0 \times 10^{-3} \text{ M}; \quad [\text{Cl}^-]_0 = 1.0 \text{ M} \text{ and } [\text{H}^+]_0 = 1.0 \text{ M}. \]

A straight line will be obtained when (circle the correct answer):

(i) \( \ln[\text{ClO}_3^-] \) is plotted as a function of time
(ii) \( 1/[\text{ClO}_3^-] \) is plotted as a function of time
(iii) \( [\text{ClO}_3^-] \) is plotted as a function of time
(iv) None of the above.

At \([\text{Cl}^-] >> [\text{ClO}_3^-]\) and \([\text{H}^+]_0 >> [\text{ClO}_3^-]\), \( R = k_{\text{eff}}[\text{ClO}_3^-] \) - pseudo first order kinetics
Enzyme $E$ reacts with substrate $S$ according to the mechanism:

$$E + S \leftrightarrow ES \quad k_1,k_{-1}$$

$$ES \rightarrow P + E \quad k_2$$

The rate of appearance of product $P$ is $R$. The kinetics is described by the Michaelis-Menten equation, which can be expressed as:

$$R = \frac{k_2[E_0][S]}{[S] + k_m} \quad k_m = \frac{k_{-1} + k_2}{k_1}$$

(a) How can you determine $k_m$ from measuring $R$ as a function of $[S]$?
A plot of $1/R$ vs $1/[S]$ will give a straight line. Slope=$k_m/(k_2[E]_0)$, intercept=$1/(k_2[E]_0)$, slope/intercept=$k_m$

(b) What is $R_{\text{max}}$, the maximum value of $R$ that can be obtained in a reaction carried out with initial concentration of enzyme $[E_0]$, and at what concentration of $[S]$ it will be obtained?
At very large $[S]$ (or $[S] \gg k_m$)

$$\frac{1}{R} = \frac{1}{k_2[E_0]} \left(1 + \frac{k_m}{[S]}\right) \approx \frac{1}{k_2[E_0]}$$

$$R_{\text{max}} = k_2[E_0]$$

(c) Show that when $[S] = k_m$, the value of $R$ is half of the maximum possible value $R_{\text{max}}$.

$$\frac{R_{\text{max}}}{R} = \frac{k_2[E_0]}{k_2[E_0]} \left(1 + \frac{k_m}{[S]}\right) = 1 + \frac{k_m}{[S]} \quad R_{\text{max}}/R=2 \text{ when } k_m/[S]=1 \text{ or } k_m=[S]$$