CYL565 2014-15 Homework # 2

24/01/2015

Due on: 29/01/2015

1. An autocatalytic reaction is one where one of the products catalyses the reaction. Derive an integrated rate law for the autocatalytic reaction A $\longrightarrow$ P given that $-\,\mathrm{d[A]}/\,\mathrm{d}t = k\mathrm{[A][P]}$ and initial $\mathrm{[A]} = a$, $\mathrm{[P]} = p$.

2. For the reaction A $\rightleftharpoons$ B, why is $-\,\mathrm{d[A]_{eq}}/\,\mathrm{d}t = 0$, not a steady state?

3. For the conversion of A to P by the mechanism A $\xrightarrow{k_1}$ I $\xrightarrow{k_2}$ P, obtain expressions for [A], [I], and [P] in the limiting case when $k_1 \ll k_2$. Hence decide whether the two-step mechanism can be differentiated from a one-step mechanism in this limit.

4. This question requires the use of a spreadsheet program. Consider a consective reaction A $\xrightarrow{k_1}$ I $\xrightarrow{k_2}$ P. Plot (a) $\mathrm{[A]}(t)$, $\mathrm{[I]}(t)$, $\mathrm{[P]}(t)$, and (b) $\mathrm{d[A]}/\mathrm{d}t(t)$, $\mathrm{d[I]}/\mathrm{d}t(t)$, and $\mathrm{d[P]}/\mathrm{d}t(t)$ vs. time profiles for three cases: $k_1 = k_2 = 1\,\mathrm{s}^{-1}$; $k_1 = 1\,\mathrm{s}^{-1}, k_2 = 10\,\mathrm{s}^{-1}$; $k_1 = 10\,\mathrm{s}^{-1}, k_2 = 1\,\mathrm{s}^{-1}$. In the case where the SSA holds, decide whether your plot indicates that setting $\mathrm{d[I]}/\mathrm{d}t(t) = 0$ is justified.

5. This question is once again on the paper "Time-Resolved Resonance Fluorescence Study of Electronically Excited Iodine Atoms." Under what conditions does the proposed mechanism $\mathrm{I}(5\,^2\mathrm{P}_{1/2}) + \text{alkene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{complex} \xrightarrow{k_2} \mathrm{I}(5\,^2\mathrm{P}_{1/2}) + \text{alkene}$ agree with the observed rate law for the quenching of iodine fluorescence by alkene. How is k_q related to the rate constants in the proposed mechanism?

6. The chlorination of an organic molecule (M) to give P may proceed by the following mechanism: (i) $\mathrm{Cl_2} \xrightarrow{k_1} 2\,\mathrm{Cl}$ (ii) $\mathrm{Cl} + \mathrm{M} \xrightarrow{k_2} \mathrm{R}$ (iii) $\mathrm{R} + \mathrm{Cl_2} \xrightarrow{k_3} \mathrm{P} + \mathrm{Cl}$ (iv) $\mathrm{Cl} + \mathrm{Cl} \xrightarrow{k_4} \mathrm{Cl_2}$. (a) Setup the rate expressions for Cl, R, and P. (b) Apply the steady state approximation to the intermediate species and obtain the rate law.