assignment 1

(due before class on 16 Oct 2020)

1. Consider the first-order reversible reaction involving two steps : $\mathrm{A}_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{A}_3$

Assuming that initially at time $t = 0$, $[A_1] = [A_1]_0$ and $[A_2]_0 = [A_3]_0 = 0$, obtain expressions for $[A_1]$, $[A_2]$ and $[A_3]$ and the equilibrium constant for the overall reaction $\mathrm{A}_1 \rightleftharpoons \mathrm{A}_3$

2. The reaction A+B→C+D takes place in two steps, by the following mechanism :

$$2\mathrm{A} \rightleftarrows \mathrm{D}$$

$$\mathrm{B}+\mathrm{D} \overset{k_2}{\rightarrow} \mathrm{A}+\mathrm{C}$$

The first step comes to a rapid equilibrium (constant K_1). Obtain rate of formation of C in terms of K_1, k_2 and $[A]$ and $[B]$.

3. A reaction has the stoichiometry 2A + 2B→ Y + 2Z; rate of reaction, $v = k\,[A]^{\alpha}\,[B]^{\beta}$

Some results for the rate of consumption of A are shown below:

$[\mathrm{A}]/\mathrm{mol\ dm^{-3}}$	$[\mathrm{B}]/\mathrm{mol\ dm^{-3}}$	$v/\mathrm{mol\ dm^{-3}s^{-1}}$
1.4×10^{-2}	2.3×10^{-2}	7.4×10^{-9}
2.8×10^{-2}	4.6×10^{-2}	5.92×10^{-8}
2.8×10^{-1}	4.6×10^{-2}	5.92×10^{-6}

Deduce α and β and the rate constant k.

4. (a) Integrate the rate equation for an autocatalytic reaction of the form A→ P, with rate law $v = k[A][P]$, and show that

or, $\frac{[P]}{[P]_0} = \frac{(1+b)e^{at}}{1+be^{at}}$, where $a = ([\mathrm{A}]_0 + [\mathrm{P}]_0)\,k$ and $b = \frac{[\mathrm{P}]_0}{[\mathrm{A}]_0}$

(b) Plot $\frac{[P]}{[P]_0}$ against $a.t$ for several values of b. Discuss the effect of autocatalysis on the shape of a plot of $\frac{[P]}{[P]_0}$ against t by comparing your results with those for a first-order process, (c) Show that the reaction rate reaches a maximum at $t_{\max} = -\frac{1}{a}\ln b$.