Chemistry 4000/5000/7001, Fall 2012, Assignment 7

Due: Friday, November 9, 4:00 p.m.
Total marks: 28

In this assignment, you will analyze a master equation for a very simple model of a chemical reaction. Suppose that we have n equally spaced non-degenerate energy levels with spacing ΔE between adjacent levels. Molecules make transitions between adjacent levels only (Landau-Teller approximation) with transition rates w_{ij}. Once the molecule reaches the n'th level, it can form a product irreversibly with transition rate w_p.

1. Let $P_i(t)$ be the probability of being in state i at time t. Write down the master equation for this model. [3 marks]

   Note: You will need to treat the lowest energy level and the n'th energy level as special cases.

2. Suppose that for all the upward transitions, $w_{ij} = w_+$ is a constant. What is w_-, the transition rate for the downward transitions? [1 mark]

   Bonus: The "expected" answer requires an assumption. What is that assumption?

3. In the rest of this assignment, fix $n = 5$, take $w_+ = 10^7\,\mathrm{s}^{-1}$, $w_p = 10^6\,\mathrm{s}^{-1}$, $\Delta E = 10^{-21}$ J and $T = 700\,\mathrm{K}$. Calculate w_-. [2 marks]

4. The solution of the master equation with initial condition $P_1(0) = 1$, $P_2(0) = 0$, $P_3(0) = 0$, $P_4(0) = 0$ and $P_5(0) = 0$ is

$$
\begin{aligned}
P_1(t) &= 0.036e^{\lambda_1 t} + 0.129e^{\lambda_2 t} + 0.242e^{\lambda_3 t} + 0.271e^{\lambda_4 t} + 0.323e^{\lambda_5 t}\\
P_2(t) &= -0.091e^{\lambda_1 t} - 0.206e^{\lambda_2 t} - 0.106e^{\lambda_3 t} + 0.241e^{\lambda_4 t} + 0.162e^{\lambda_5 t}\\
P_3(t) &= 0.107e^{\lambda_1 t} + 0.008e^{\lambda_2 t} - 0.278e^{\lambda_3 t} + 0.210e^{\lambda_4 t} - 0.048e^{\lambda_5 t}\\
P_4(t) &= -0.084e^{\lambda_1 t} + 0.181e^{\lambda_2 t} - 0.060e^{\lambda_3 t} + 0.180e^{\lambda_4 t} - 0.218e^{\lambda_5 t}\\
P_5(t) &= 0.032e^{\lambda_1 t} - 0.116e^{\lambda_2 t} + 0.217e^{\lambda_3 t} + 0.151e^{\lambda_4 t} - 0.284e^{\lambda_5 t}
\end{aligned}
$$

with

$$\begin{aligned}
\lambda_1 &= -3.817 \times 10^7\,\mathrm{s}^{-1}\\
\lambda_2 &= -2.775 \times 10^7\,\mathrm{s}^{-1}\\
\lambda_3 &= -1.487 \times 10^7\,\mathrm{s}^{-1}\\
\lambda_4 &= -1.433 \times 10^5\,\mathrm{s}^{-1}\\
\lambda_5 &= -4.430 \times 10^6\,\mathrm{s}^{-1}
\end{aligned}$$

(a) Verify that this solution satisfies the initial condition (taking into account the finite precision of the data). [3 marks]

(b) Verify that the solution satisfies the equation for dP_1/dt.

(You could of course also verify the other equations. I just want to see that you understand how the solutions are related to the differential equations, which is why I'm just asking you to verify one particular component.) [7 marks]

(c) Obtain the probability distribution for the time of reaction. [6 marks]

(d) Calculate the rate constant for this reaction. [6 marks]