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

1.

$$\begin{aligned}
\frac{dP_1}{dt} &= w_-P_2 - w_+P_1 \\
\frac{dP_i}{dt} &= w_+P_{i-1} + w_-P_{i+1} - (w_+ + w_-)P_i \qquad \text{for } i = 2, \ldots, n-1 \\
\frac{dP_n}{dt} &= w_+P_{n-1} - (w_- + w_p)P_n
\end{aligned}$$

2. In class, we derived the relationship

$$\frac{w_+}{w_-} = \exp\left(\frac{-\Delta E}{k_BT}\right)$$

assuming that the system eventually reaches equilibrium. The latter is the assumption: This system will not reach equilibrium since reaction in this model is an irreversible process. Formally then, there are no constraints on w_+ and w_-. The assumption of irreversible reaction violates the law of microscopic reversibility, so that assumption is the real problem. If we allowed for reversibility of the reaction, the ratio of w_+ to w_- would again be constrained to obey the Boltzmann relationship.

In any event, this gives

$$w_- = w_+ \exp\left(\frac{\Delta E}{k_BT}\right).$$

3.

$$\begin{aligned}
w_- &= (10^7\,\mathrm{s}^{-1}) \exp\left(\frac{10^{-21}\,\mathrm{J}}{(1.380\,6488 \times 10^{-23}\,\mathrm{J\,K^{-1}})(700\,\mathrm{K})}\right) \\
&= 1.11 \times 10^7\,\mathrm{s}^{-1}
\end{aligned}$$

4. (a) If we evaluate the solution at $t = 0$, we get

$$\begin{aligned}
P_1(0) &= 0.036 + 0.129 + 0.242 + 0.271 + 0.323 = 1.001 \approx 1 \\
P_2(t) &= -0.091 - 0.206 - 0.106 + 0.241 + 0.162 = 0 \\
P_3(t) &= 0.107 + 0.008 - 0.278 + 0.210 - 0.048 = -0.001 \approx 0 \\
P_4(t) &= -0.084 + 0.181 - 0.060 + 0.180 - 0.218 = -0.001 \approx 0 \\
P_5(t) &= 0.032 - 0.116 + 0.217 + 0.151 - 0.284 = 0
\end{aligned}$$

(b) The trick is to show that the left- and right-hand sides are equal (within the precision of the data):

$$\begin{aligned}
\text{LHS} &= \frac{dP_1}{dt} \\
&= \frac{d}{dt}\left(0.036e^{\lambda_1 t} + 0.129e^{\lambda_2 t} + 0.242e^{\lambda_3 t} + 0.271e^{\lambda_4 t} + 0.323e^{\lambda_5 t}\right) \\
&= 0.036(-3.817 \times 10^7\,\mathrm{s}^{-1})e^{\lambda_1 t} + 0.129(-2.775 \times 10^7\,\mathrm{s}^{-1})e^{\lambda_2 t} \\
&\quad + 0.242(-1.487 \times 10^7\,\mathrm{s}^{-1})e^{\lambda_3 t} + 0.271(-1.433 \times 10^5\,\mathrm{s}^{-1})e^{\lambda_4 t} \\
&\quad + 0.323(-4.430 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_5 t} \\
&= -(1.4 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_1 t} - (3.58 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_2 t} - (3.60 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_3 t} \\
&\quad - (3.88 \times 10^4\,\mathrm{s}^{-1})e^{\lambda_4 t} - (1.43 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_5 t} \\
\text{RHS} &= w_- P_2 - w_+ P_1 \\
&= (1.11 \times 10^7\,\mathrm{s}^{-1})\left(-0.091e^{\lambda_1 t} - 0.206e^{\lambda_2 t} - 0.106e^{\lambda_3 t} + 0.241e^{\lambda_4 t} + 0.162e^{\lambda_5 t}\right) \\
&\quad - (10^7\,\mathrm{s}^{-1})\left(0.036e^{\lambda_1 t} + 0.129e^{\lambda_2 t} + 0.242e^{\lambda_3 t} + 0.271e^{\lambda_4 t} + 0.323e^{\lambda_5 t}\right) \\
&= -(1.4 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_1 t} - (3.58 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_2 t} - (3.60 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_3 t} \\
&\quad - (3 \times 10^4\,\mathrm{s}^{-1})e^{\lambda_4 t} - (1.43 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_5 t}
\end{aligned}$$

Within the precision of the calculation, the left- and right-hand sides agree, which verifies the solution.

(c) The probability that the molecule hasn't reacted at time t is

$$\begin{aligned}
P_{\text{unreacted}} &= P_1 + P_2 + P_3 + P_4 + P_5 \\
&= 0e^{\lambda_1 t} - 0.004e^{\lambda_2 t} + 0.015e^{\lambda_3 t} + 1.053e^{\lambda_4 t} - 0.065e^{\lambda_5 t} \\
\therefore P_{\text{reacted}} &= 1 - P_{\text{unreacted}} \\
&= 1 + 0.004e^{\lambda_2 t} - 0.015e^{\lambda_3 t} - 1.053e^{\lambda_4 t} + 0.065e^{\lambda_5 t}
\end{aligned}$$

P_{reacted} is the cumulative probability distribution for the reaction time. The probability distribution for the reaction time is therefore

$$\begin{aligned}
p_r(t) &= \frac{dP_{\text{reacted}}}{dt} \\
&= 0.004(-2.775 \times 10^7\,\mathrm{s}^{-1})e^{\lambda_2 t} - 0.015(-1.487 \times 10^7\,\mathrm{s}^{-1})e^{\lambda_3 t} \\
&\quad - 1.053(-1.433 \times 10^5\,\mathrm{s}^{-1})e^{\lambda_4 t} + 0.065(-4.430 \times 10^6\,\mathrm{s}^{-1})e^{\lambda_5 t} \\
&= -(1.11 \times 10^5\,\mathrm{s}^{-1})e^{\lambda_2 t} + (2.231 \times 10^5\,\mathrm{s}^{-1})e^{\lambda_3 t} + (1.509 \times 10^5\,\mathrm{s}^{-1})e^{\lambda_4 t} \\
&\quad - (2.880 \times 10^5\,\mathrm{s}^{-1})e^{\lambda_5 t}
\end{aligned}$$

(Note that I'm not rounding to the correct number of significant figures here because I'm going to carry this equation into the next calculation.)

(d) The average reaction time is given by

$$\langle t \rangle = \int_0^\infty t p_r(t)\, dt$$

This will give us a set of integrals of the form $\int te^{\lambda_i t}\,dt$. You can either (a) evaluate this integral by parts, (b) look it up in a table of integrals, or (c) get Maple to evaluate it for you.(For exams, you are only expected to know elementary integrals. Should you need any other integrals, I would put them on the formula sheet.) The result is

$$\int_0^\infty te^{\lambda_i t}\,dt = \frac{1}{\lambda_i^2}(\lambda_i t - 1)e^{\lambda_i t}\Big|_0^\infty = \frac{1}{\lambda_i^2}$$

since $\lambda_i < 0\ \forall i$. Thus,

$$\begin{aligned}
\langle t\rangle &= \frac{-1.11\times10^5\,\mathrm{s}^{-1}}{(-2.775\times10^7\,\mathrm{s}^{-1})^2} + \frac{2.231\times10^5\,\mathrm{s}^{-1}}{(-1.487\times10^7\,\mathrm{s}^{-1})^2} + \frac{1.509\times10^5\,\mathrm{s}^{-1}}{(-1.433\times10^5\,\mathrm{s}^{-1})^2}\\
&\quad - \frac{2.880\times10^5\,\mathrm{s}^{-1}}{(-4.430\times10^6\,\mathrm{s}^{-1})^2}\\
&= 7.335\times10^{-6}\,\mathrm{s}\\
\therefore k &= \frac{1}{\langle t\rangle} = 1.4\times10^5\,\mathrm{s}^{-1}.
\end{aligned}$$