18.27 CHEM 450 HW9 Hardin Solutions

We cannot use rate-limiting step here, as $k_1 \approx k_2$ (good rule of thumb: 2 orders of magnitude)

We must use the concentrations derived in class for a sequential reaction: $A \leftrightarrow Br$, $I \leftrightarrow J$, and $P \rightarrow k$.

$$[Br](t) = [Br]_0 e^{-k_1 t}$$

$$[J](t) = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[Br]_0$$

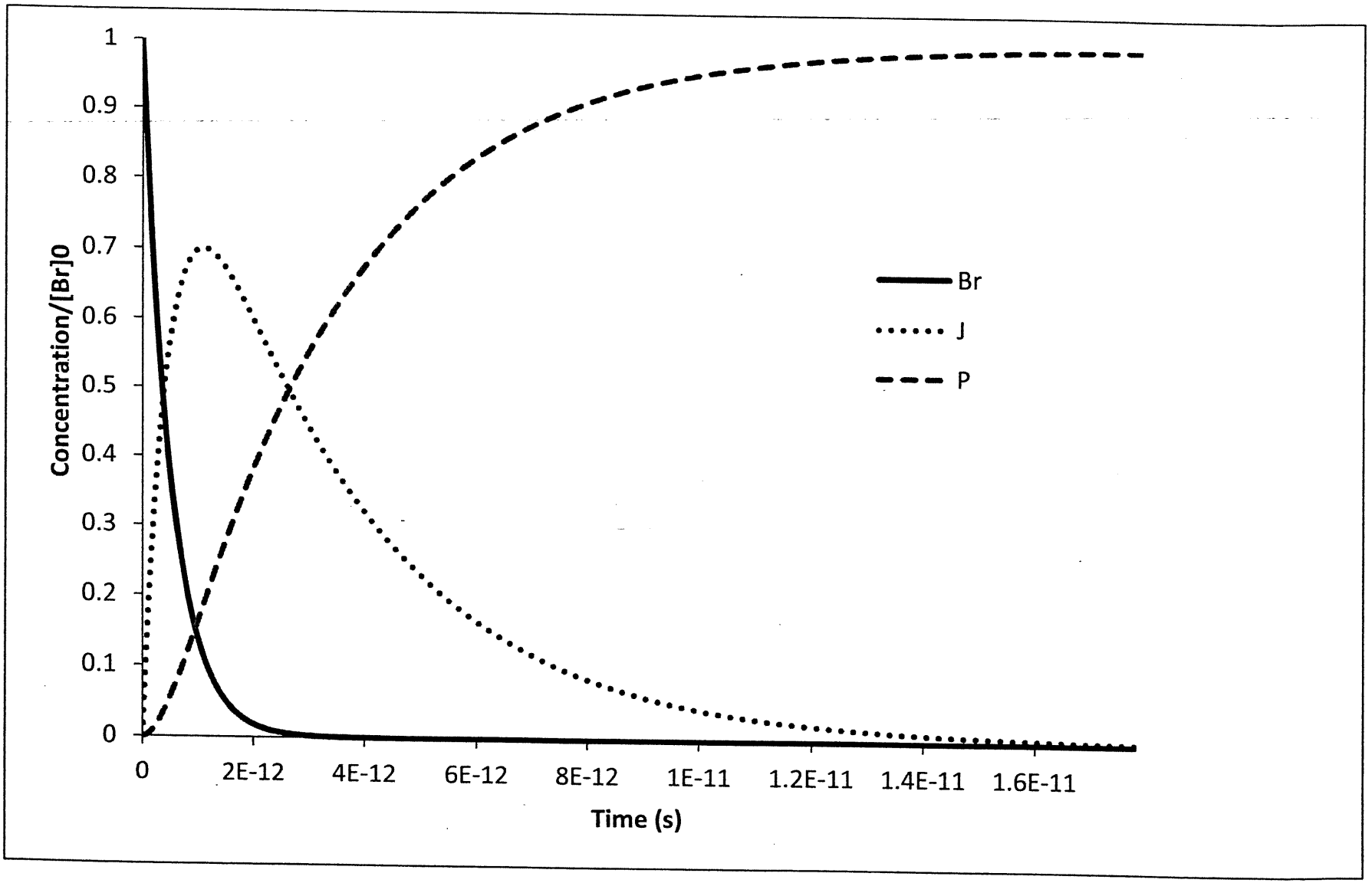
$$[P](t) = \left(\frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} + 1\right)[Br]_0$$

Which are plotted ($\frac{[Br]}{[Br]_0}$, $\frac{[J]}{[Br]_0}$, and $\frac{[P]}{[Br]_0}$) on the next page.

for a, we use eqn. 35,57

$$t_{max} = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right) = \frac{1}{2.0\times10^{12}\,s^{-1} - 3.3\times10^{11}\,s^{-1}}\ln\left(\frac{2.0\times10^{12}\,s^{-1}}{3.3\times10^{11}\,s^{-1}}\right)$$

$$\boxed{t_{max} = 1.079\times10^{-12}\,s}$$


Concentration/[Br]0
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2E-12
4E-12
6E-12
8E-12
1E-11
1.2E-11
1.4E-11
1.6E-11
Time (s)
Br
J
P

P19.2

a) rate = $\frac{d[N_2]}{dt} = k[NO]^2[H_2]^2$ - not consistent as a single step as written - implies H_2 is second order.

b) now, rate = $\frac{d[N_2]}{dt} = k_2[H_2][N_2O]$, but $[N_2O]$ is an intermediate. use SSA:

$$\frac{d[N_2O]}{dt} = k_1[H_2][NO]^2 - k_2[H_2][N_2O] = 0$$

$$[N_2O] = \frac{k_1}{k_2}\frac{[H_2][NO]^2}{[H_2]} = \frac{k_1}{k_2}[NO]^2$$

meaning

rate = $\frac{d[N_2]}{dt} = k_1[H_2][NO]^2$ so yes - this one is consistent with experiment.

c) This time, we have a fast eqm: we can use the PE approximation to get $[N_2O_2]$, then SSA to get $[N_2O]$

overall: rate = $\frac{d[N_2]}{dt} = k_3[H_2][N_2O]$

PE: $\frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2} \Rightarrow [N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$

SSA: $\frac{d[N_2O]}{dt} \approx 0 = k_2[H_2][N_2O_2] - k_3[H_2][N_2O]$

$$[N_2O] = \frac{k_2}{k_3}[N_2O_2]$$

thus overall, rate $= \left(k_3[H_2]\right)\left(\frac{k_2}{k_3}[N_2O_2]\right)$

$= \frac{k_2 k_1}{k_{-1}}[H_2][NO]^2$

Lessons learned:

1) sometimes more than one mechanism can describe a rate law consistent with experiment.

2) Sometimes it is necessary to deal with more than one intermediate. It is ok to use <u>both</u> PE and SSA in the same mechanism.