ChemE 2200 - Physical Chemistry II for Engineers - Spring 2025
Solution to Homework Assignment 11

1. To compare the rates, we need a rate equation for each reaction. For all reactions, the rate of formation of C is given by the second elementary reaction.

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \qquad (1)$$

We need expressions for the intermediate B for each reaction.

Reaction I. Apply the steady-state approximation to B. This is justified because $k_2 = A_2e^{-2.5} = A_2(0.08)$ » $k_1 = A_1e^{-15} = A_1(3 \times 10^{-7})$. We will assume the pre-exponentials A_1, A_{-1}, and A_2 are approximately equal, in this reaction mechanism and in the subsequent reaction mechanisms.

$$\frac{d[\mathrm{B}]}{dt} = 0 = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}]$$

$$[\mathrm{B}] = \frac{k_1}{k_{-1}+k_2}[\mathrm{A}] \approx \frac{k_1}{k_2}[\mathrm{A}] \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{A}] = A_1(3\times10^{-7})[\mathrm{A}]$$

Reaction II. Apply the pre-equilibrium approximation. This is justified because $k_1 = A_1e^{-5} = \mathrm{A}_1(0.007)$ » $k_2 = A_2e^{-20} = A_2(2 \times 10^{-9})$.

$$k_1[\mathrm{A}] = k_{-1}[\mathrm{B}]$$

$$[\mathrm{B}] = \frac{k_1}{k_{-1}}[\mathrm{A}] \qquad (4)$$

Substitute eqn (3) into eqn (1).

$$\frac{d[\mathrm{C}]}{dt} = \frac{k_1k_2}{k_{-1}}[\mathrm{A}] = \frac{A_1A_2}{A_{-1}}\mathrm{e}^{-(E_{\mathrm{a},1}+E_{\mathrm{a},2}-E_{\mathrm{a},-1})/RT}[\mathrm{A}] = \frac{A_1A_2}{A_{-1}}\mathrm{e}^{-(5+20-5)}[\mathrm{A}] = \frac{A_1A_2}{A_{-1}}(2\times10^{-9})[\mathrm{A}]$$

Reaction III. Apply the steady-state approximation to B. This is justified because $k_{-1} = A_{-1}e^{-2.5} = A_{-1}(0.08)$ » $k_1 = A_1e^{-10} = A_1(5 \times 10^{-5})$.

$$\frac{d[\mathrm{B}]}{dt} = 0 = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] - k_2[\mathrm{B}]$$

$$[\mathrm{B}] = \frac{k_1}{k_{-1}+k_2}[\mathrm{A}] \approx \frac{k_1}{k_{-1}}[\mathrm{A}] \qquad (5)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{C}]}{dt} = \frac{k_1k_2}{k_{-1}}[\mathrm{A}] = \frac{A_1A_2}{A_{-1}}\mathrm{e}^{-(E_{\mathrm{a},1}+E_{\mathrm{a},2}-E_{\mathrm{a},-1})/RT}[\mathrm{A}] = \frac{A_1A_2}{A_{-1}}\mathrm{e}^{-(10+10-2.5)}[\mathrm{A}] = \frac{A_1A_2}{A_{-1}}(3\times10^{-8})[\mathrm{A}]$$

Reaction I produces C at the highest rate, by a factor of about 10. Note: this prediction depends on the ratio of the pre-exponentials A_2 and A_{-1}. If $A_2/A_{-1} < 10$, the prediction is reasonable. But if $A_2/A_{-1} > 10$, then Reaction III produces A at the highest rate.

The prediction that Reaction I is the fastest is consistent with a qualitative examination of the reaction-coordinate energy-level diagrams. Reaction I has the lowest maximum energy barrier and the energy level for B is not in a deep hole. For example, if the energy level for B in Reaction I were below 0 energy units, the barrier to C would be the largest barrier of all steps in reactions I, II, and III.

2.(A) Begin with a rate equation for NO_2.

$$\begin{aligned}\frac{d[NO_2]}{dt} &= k_1[N_2O_5] - k_{-1}[NO_2][NO_3] + 2k_2[NO][NO_3] \\ &= k_1[N_2O_5] + [NO_3](2k_2[NO] - k_{-1}[NO_2]) \qquad (1)\end{aligned}$$

We need an expression for the concentration of the intermediate NO_3. Apply the steady-state approximation to NO_3 and solve for $[NO_3]$.

$$\frac{d[NO_3]}{dt} = 0 = k_1[N_2O_5] - k_{-1}[NO_2][NO_3] - k_2[NO][NO_3]$$

$$[NO_3](k_{-1}[NO_2] + k_2[NO]) = k_1[N_2O_5]$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2]+k_2[NO]} \qquad (2)$$

Use eqn (2) to substitute for $[NO_3]$ in eqn (1).

$$\begin{aligned}\frac{d[NO_2]}{dt} &= k_1[N_2O_5] + \frac{k_1[N_2O_5]}{k_{-1}[NO_2]+k_2[NO]}(2k_2[NO] - k_{-1}[NO_2]) \\ &= k_1[N_2O_5]\left[1 + \frac{2k_2[NO] - k_{-1}[NO_2]}{k_{-1}[NO_2]+k_2[NO]}\right] \\ &= k_1[N_2O_5]\left[\frac{k_{-1}[NO_2]+k_2[NO] + 2k_2[NO] - k_{-1}[NO_2]}{k_{-1}[NO_2]+k_2[NO]}\right]\end{aligned}$$

$$\frac{d[NO_2]}{dt} = \frac{3k_1k_2[N_2O_5][NO]}{k_{-1}[NO_2]+k_2[NO]} \qquad \text{rate equation with steady-state approximation}$$

(B) Assume pre-equilibrium, which yields the following relation:

$$k_{-1}[NO_2][NO_3] = k_1[N_2O_5]$$

$$[NO_3] = \frac{k_1[N_2O_5]}{k_{-1}[NO_2]} \qquad (3)$$

Use eqn (3) to substitute for $[NO_3]$ in eqn (1).

$$\begin{aligned}\frac{d[NO_2]}{dt} &= k_1[N_2O_5] + \frac{k_1[N_2O_5]}{k_{-1}[NO_2]}(2k_2[NO] - k_{-1}[NO_2]) \\ &= k_1[N_2O_5]\left[1 + \frac{2k_2[NO] - k_{-1}[NO_2]}{k_{-1}[NO_2]}\right] \\ &= k_1[N_2O_5]\left[\frac{k_{-1}[NO_2] + 2k_2[NO] - k_{-1}[NO_2]}{k_{-1}[NO_2]}\right]\end{aligned}$$

$$\frac{d[NO_2]}{dt} = \frac{2k_1k_2[N_2O_5][NO]}{k_{-1}[NO_2]} \qquad \text{rate equation with pre-equilibrium}$$

(C) one method: use chemistry. Measure the rate of the reaction as a function of [NO]. If the reaction is first order with respect to [NO] at low concentration and decreases to zero order at high concentration, then it is valid to assume NO_3 is at steady state. If the rate is uniformly first order, then pre-equilibrium is valid.

another method: use spectroscopy. Measure $[NO_3]$ with infrared or UV-visible spectroscopy. Is the concentration low enough to justify the steady-state approximation?

3. The rate equation provides some clues. $[OH^-]$ is in the denominator, so we suspect OH^- opposes the forward reaction. Thus the first reaction must be reversible and the first reaction (forward and/or reverse) must be fast, relative to some subsequent reaction. That is, $k_1 + k_{-1} \gg k_2$ and/or $k_1 + k_{-1} \gg k_3$.

   We also note that $[OH^-]$ is not in the numerator, so we suspect reaction 3 is not the rate-limiting step.

   Assume the first reaction is reversible and is in equilibrium.

$$k_1[OCl^-][H_2O] = k_{-1}[HOCl][OH^-]$$

$$[HOCl] = \frac{k_1[OCl^-][H_2O]}{k_{-1}[OH^-]} = K_{eq,1}\frac{[OCl^-][H_2O]}{[OH^-]} \qquad (1)$$

   Assume the second reaction is rate-limiting; $k_1 + k_{-1} \gg k_2$. Thus the overall rate is equal to the rate of the second reaction.

$$\frac{d[Cl^-]}{dt} = k_2[HOCl][I^-] \qquad (2)$$

   Substitute equation (1) into equation (2).

$$\frac{d[Cl^-]}{dt} = k_2[HOCl][I^-] = k_2K_{eq,1}\frac{[OCl^-][H_2O]}{[OH^-]}[I^-] = k_2K_{eq,1}[H_2O]\frac{[OCl^-][I^-]}{[OH^-]}$$

   In summary, the mechanism is

$$OCl^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HOCl + OH^- \qquad \text{in equilibrium}$$

$$HOCl + I^- \xrightarrow{k_2} HOI + Cl^- \qquad \text{slow and rate limiting}$$

$$HOI + OH^- \xrightarrow{k_3} OI^- + H_2O \qquad \text{fast}$$

   and the rate constant k is

$$k = k_2K_{eq,1}[H_2O]$$

4. The rate equation suggests that the rate-limiting step involves the reaction of B alone. The products of this first reaction are not important. Whatever forms in this rate-limiting step reacts quickly with A to form products Y and Z. Let's propose a hypothetical intermediate X.

$$B \xrightarrow{k_1} X \qquad \text{rate-limiting}$$

$$X + A \xrightarrow{k_2} Y + Z \qquad \text{rapid}$$

   Use the second reaction to write a rate equation for Z.

$$\frac{d[Z]}{dt} = k_2[X][A] \qquad (1)$$

   Apply the steady-state approximation to X.

$$\frac{d[X]}{dt} = 0 = k_1[B] - k_2[X][A]$$

$$k_2[X][A] = k_1[B] \qquad (2)$$

   Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{Z}]}{dt} = k_1[\mathrm{B}]$$

This is the correct form for the rate equation and $k = k_1$. The observed rate equation is also obtained with the following mechanism.

$$\mathrm{B} \overset{k_1}{\rightarrow} \mathrm{X} + \mathrm{Y} \qquad \text{rate-limiting}$$

$$\mathrm{X} + \mathrm{A} \overset{k_2}{\rightarrow} \mathrm{Z} \qquad \text{rapid}$$

5. Try a simple mechanism. Assume the overall reaction is elementary as written.

$$(\mathrm{Hg}_2)^{2+} + \mathrm{Tl}^{3+} \overset{k_1}{\rightarrow} \mathrm{Hg}^{2+} + \mathrm{Hg}^{2+} + \mathrm{Tl}^{+}$$

This mechanism yields the following rate equation.

$$\frac{d[\mathrm{Tl}^+]}{dt} = k_1[(\mathrm{Hg}_2)^{2+}][\mathrm{Tl}^{3+}]$$

This is the numerator of the observed rate equation. We need to add a reaction in which Hg^{2+} opposes the progress of the overall reaction. If the reaction above were reversible, Hg^{2+} would oppose the overall reaction progress. But the reverse reaction would require a ternary encounter, which is improbable. We need Hg^{2+} to react to form a reactant or an intermediate that leads to a reactant. That is, we need to balance the reaction $\mathrm{Hg}^{2+} \rightarrow (\mathrm{Hg}_2)^{2+}$. This suggests the reversible reaction

$$(\mathrm{Hg}_2)^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Hg}^{2+} + \mathrm{Hg}^{0}$$

To complete the overall reaction we must convert Hg^0 to Hg^{2+}. Create a reaction with the other reactant, Tl^{3+}.

$$\mathrm{Hg}^0 + \mathrm{Tl}^{3+} \overset{k_2}{\rightarrow} \mathrm{Hg}^{2+} + \mathrm{Tl}^{+}$$

Derive the rate equation for this mechanism. The rate is given by the second elementary step.

$$\frac{d[\mathrm{Tl}^+]}{dt} = k_2[\mathrm{Hg}^0][\mathrm{Tl}^{3+}] \qquad (1)$$

We need an expression for the concentration of the intermediate, $[\mathrm{Hg}^0]$. Apply the steady-state approximation to Hg^0 and solve for $[\mathrm{Hg}^0]$.

$$\frac{d[\mathrm{Hg}^0]}{dt} = 0 = k_1[(\mathrm{Hg}_2)^{2+}] - k_{-1}[\mathrm{Hg}^{2+}][\mathrm{Hg}^0] - k_2[\mathrm{Hg}^0][\mathrm{Tl}^{3+}]$$

$$[\mathrm{Hg}^0] = \frac{k_1[(\mathrm{Hg}_2)^{2+}]}{k_{-1}[\mathrm{Hg}^{2+}] + k_2[\mathrm{Tl}^{3+}]} \qquad (2)$$

Substitute eqn (2) into eqn (1).

$$\frac{d[\mathrm{Tl}^+]}{dt} = k_2 \frac{k_1[(\mathrm{Hg}_2)^{2+}]}{k_{-1}[\mathrm{Hg}^{2+}] + k_2[\mathrm{Tl}^{3+}]}[\mathrm{Tl}^{3+}] = \frac{k_1 k_2[(\mathrm{Hg}_2)^{2+}][\mathrm{Tl}^{3+}]}{k_{-1}[\mathrm{Hg}^{2+}] + k_2[\mathrm{Tl}^{3+}]}$$

This is close to the observed rate equation. We need to fix the denominator. To remove the $k_2[\mathrm{Tl}^{3+}]$ term, we assume $k_{-1}[\mathrm{Hg}^{2+}]$ is much larger than $k_2[\mathrm{Tl}^{3+}]$. We abandon the steady-state approximation on Hg^0, apply pre-equilibrium, and solve for $[\mathrm{Hg}^0]$.

$$k_1[(\mathrm{Hg}_2)^{2+}] = k_{-1}[\mathrm{Hg}^{2+}][\mathrm{Hg}^0]$$

$$[\mathrm{Hg}^0] = \frac{k_1[(\mathrm{Hg}_2)^{2+}]}{k_{-1}[\mathrm{Hg}^{2+}]} \qquad (3)$$

Substitute eqn (3) into eqn (1).

$$\frac{d[\mathrm{Tl}^+]}{dt} = k_2\,\frac{k_1[(\mathrm{Hg}_2)^{2+}]}{k_{-1}[\mathrm{Hg}^{2+}]}[\mathrm{Tl}^{3+}] = \frac{k_1 k_2}{k_{-1}}\,\frac{[(\mathrm{Hg}_2)^{2+}][\mathrm{Tl}^{3+}]}{[\mathrm{Hg}^{2+}]}$$

This agrees with the observed rate equation.

In summary, the mechanism of elementary steps is

$$(\mathrm{Hg}_2)^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Hg}^{2+} + \mathrm{Hg}^0 \qquad \text{in equilibrium}$$

$$\mathrm{Hg}^0 + \mathrm{Tl}^{3+} \xrightarrow{k_2} \mathrm{Hg}^{2+} + \mathrm{Tl}^+ \qquad \text{rate limiting}$$

6.(A) The first reaction is in equilibrium. It does not contribute to the net reaction. To show this, we rewrite the reversible reaction as follows and add the reactions.

$$\begin{array}{c} \mathrm{M} + \mathrm{I}_2 \xrightarrow{k_1} 2\mathrm{I}\cdot + \mathrm{M} \\ \underline{\mathrm{M} + 2\mathrm{I}\cdot \xrightarrow{k_{-1}} \mathrm{I}_2 + \mathrm{M}} \\ 2\mathrm{M} + \mathrm{I}_2 + 2\mathrm{I}\cdot \rightarrow 2\mathrm{I}\cdot + \mathrm{I}_2 + 2\mathrm{M} \\ \textit{sum}: \quad \text{nothing} \rightarrow \text{nothing} \end{array}$$

The net sum of chemical equations 2, 3, and 4 is

$$\mathrm{I}\cdot + \mathrm{CH_3CHO} + \cdot\mathrm{CH_3CO} + \cdot\mathrm{CH_3} + \mathrm{HI} \rightarrow$$
$$\mathrm{HI} + \cdot\mathrm{CH_3CO} + \cdot\mathrm{CH_3} + \mathrm{CO} + \mathrm{CH_4} + \mathrm{I}\cdot$$

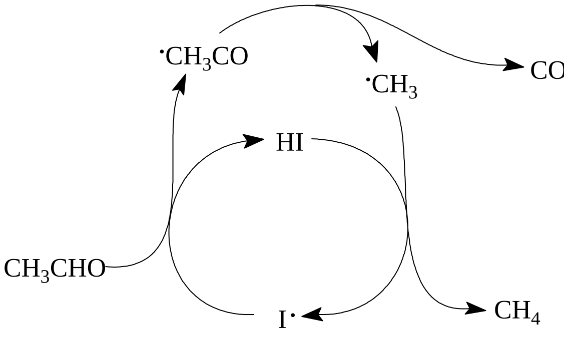
Cancel substances that appear on both sides of the chemical equation to obtain the net reaction.

$$\mathrm{CH_3CHO} \rightarrow \mathrm{CO} + \mathrm{CH_4}$$

The reaction mechanism is balanced as written.

(B) The initiation reaction is the forward reaction of reaction 1. The termination reaction is the back reaction of reaction 1. The propagation reactions are 2, 3, and 4.

(C)



(D) Begin with a rate equation from reaction 2.

$$\frac{d[\mathrm{CH_3CHO}]}{dt} = -k_2[\mathrm{I\cdot}][\mathrm{CH_3CHO}]$$

The concentration of $\mathrm{I^{\cdot}}$ is maintained by equilibrium of the 1st reaction. Use the 1st reaction to obtain an expression for $[\mathrm{I^{\cdot}}]$.

$$k_1[\mathrm{I_2}][\mathrm{M}] = k_{-1}[\mathrm{I\cdot}]^2[\mathrm{M}]$$

$$[\mathrm{I\cdot}] = \left(\frac{k_1}{k_{-1}}[\mathrm{I_2}]\right)^{1/2}$$

Thus, we obtain

$$\frac{d[\mathrm{CH_3CHO}]}{dt} = -k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\mathrm{I_2}]^{1/2}[\mathrm{CH_3CHO}]$$