ChemE 2200 – Chemical Kinetics Lecture 6

Today:

Analysis of series reactions A → B → C, cont'd

The steady-state approximation for intermediates.

"How does one identify a reactive intermediate?"

Recap: Our Goal: Given an overall reaction: $2CO + O_2 \xrightarrow{Pt} 2CO_2$

and a rate equation: $$\frac{d[CO_2]}{dt} = \frac{k_1[CO]^2}{1+k_2[CO]}$$

what is the sequence of elementary reactions?

"... not an easy task for the inexperienced."

Our Plan: Gain experience by deriving rate equations from mechanisms of elementary reactions.

First Case Study:

Overall Rxn: $A \rightarrow C$

Mechanism: $A \xrightarrow{k_1} B$

$B \xrightarrow{k_2} C$

Example:

Overall Rxn: $2NO_2Cl \rightarrow 2NO_2 + Cl_2$

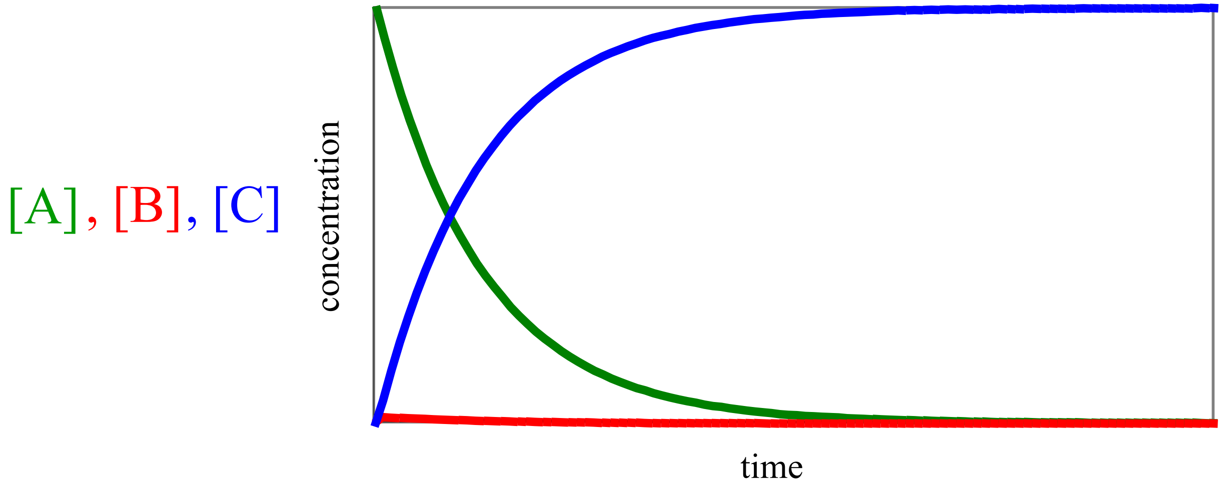
Mechanism: $NO_2Cl \rightarrow NO_2 + \bullet Cl$

$NO_2Cl + \bullet Cl \rightarrow NO_2 + Cl_2$

Recap, continued.

Mechanism of elementary reactions: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ Assume $k_2 \gg k_1$

Effect of intermediate B?



Virtually no accumulation of B.

Reaction appears to be A → C, but the mechanism requires intermediate B.

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

$$[C] \approx \left(1 - e^{-k_1 t}\right)[A]_0$$

Analysis of Series Reaction $A \rightarrow B \rightarrow C$ for $k_2 \gg k_1$

$$A \xrightarrow[\text{slow}]{k_1} B \xrightarrow[\text{fast}]{k_2} C$$

for $k_2 \gg k_1$

deductive

assume $k_2 = 1000/\text{sec}$
$k_1 = 1/\text{sec}$

inductive – better
for learning

Exact solution:

$$[A] = [A]_0 e^{-k_1 t}$$

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

$$[C] = \left[1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right][A]_0$$

Approximate [C] in the limit $k_2 \gg k_1$:

small

$= 0$ for $k_2 t \gg 1$ *i.e.*, for $t \gg 1/k_2$

$$[C] = \left[1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - \cancel{k_1}}\right][A]_0$$

$k_2 - k_1 \approx k_2$

define $1/k_2$ as the *induction period.*

$$[C] \approx \left[1 + \frac{-\cancel{k_2} e^{-k_1 t}}{\cancel{k_2}}\right][A]_0$$

$$[C] \approx (1 - e^{-k_1 t})[A]_0$$

looks like $A \xrightarrow{k_1} C$

For rxns in series,
overall rate =
rate of RLS

Analysis of Series Reaction A → B → C for k_2 » k_1, cont'd

Is [B] *relatively* small? Calculate [B]/[A].

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{\dfrac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[\cancel{\mathrm{A}}]_0}{[\cancel{\mathrm{A}}]_0\, e^{-k_1 t}}$$

assume $k_2 = 1000/\mathrm{sec}$
$k_1 = 1/\mathrm{sec}$

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} = \frac{k_1}{k_2 - \cancel{k_1}}\left(1 - e^{-(k_2 - \cancel{k_1})t}\right)$$

$k_2 - k_1 \approx k_2$

0 for t » $1/k_2$

$$\frac{[\mathrm{B}]}{[\mathrm{A}]} \approx \frac{k_1}{k_2}\left(1 - \cancel{e^{-k_2 t}}\right) \approx \frac{k_1}{k_2}$$

i.e., for t » induction period.

The ratio [B]/[A] is small and constant.

Analysis of Series Reaction A → B → C for $k_2 \gg k_1$, cont'd

Is [B] *relatively* small? Calculate [B]/[C].

0 for $t \gg 1/k_2$

$$\frac{[B]}{[C]} = \frac{\dfrac{k_1}{k_2 - \cancel{k_1}}\left(e^{-k_1 t} - \cancel{e^{-k_2 t}}\right)\cancel{[A]_0}}{\left[1 + \dfrac{\cancel{k_1 e^{-k_2 t}} - \cancel{k_2} e^{-k_1 t}}{\cancel{k_2} - \cancel{k_1}}\right]\cancel{[A]_0}} \approx \frac{\dfrac{k_1}{k_2} e^{-k_1 t}}{1 - e^{-k_1 t}} \approx \frac{k_1}{k_2}\boxed{\frac{e^{-k_1 t}}{1 - e^{-k_1 t}}}$$

$\rightarrow \infty$ at $t = 0$

< 1 for $t > \dfrac{\ln 2}{k_1}$

0

$k_2 - k_1 \approx k_2$

$$\frac{[B]}{[C]} < \frac{k_1}{k_2}$$

Ratio [B]/[C] is small.

But not necessarily constant.

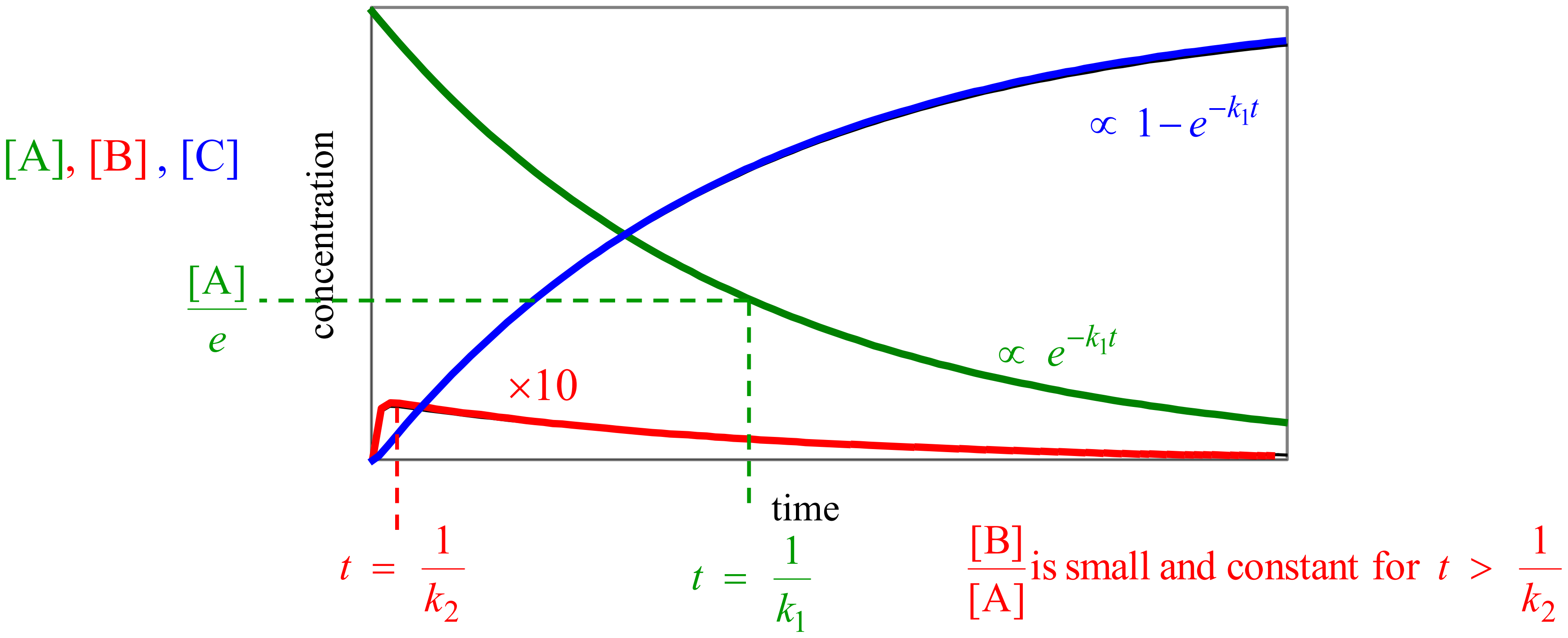
Analysis of Series Reaction A → B → C for $k_2 » k_1$, induction period $t = 1/k_2$.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$$

$$[\mathrm{B}] = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[\mathrm{A}]_0$$

$$[\mathrm{C}] = \left[1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right][\mathrm{A}]_0$$



$\frac{[\mathrm{B}]}{[\mathrm{A}]}$ is small and constant for $t > \frac{1}{k_2}$

Analysis of Series Reaction $A \rightarrow B \rightarrow C$ for $k_2 \gg k_1$, cont'd

Rather than integrate the exact solution and then approximate, it is useful to apply the approximation to the differential rate equation and then integrate.

exact: $$[B] = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)[A]_0$$

differentiate

$k_2 - k_1 \approx k_2$

$$\frac{d[B]}{dt} = \frac{k_1}{k_2 - \cancel{k_1}}\left(-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right)[A]_0$$

$$\frac{d[B]}{dt} \approx k_1\left[-\frac{k_1}{k_2}e^{-k_1 t} - \cancel{e^{-k_2 t}}\right][A]_0$$

0 for $t \gg 1/k_2$

$$\approx -\overbrace{\frac{k_1^2}{k_2}}^{\text{very small}}\underbrace{e^{-k_1 t}}_{<1}[A]_0 \approx 0$$

[B] is small and constant.

[B] is in steady state.

If the concentration of an intermediate is relatively small and constant, we may apply the Steady-State Approximation to the intermediate:

$$\frac{d[\text{intermediate}]}{dt} = 0$$

Applying the Steady-State Approximation

Calculate [C] = … for $\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$ given $k_2 \gg k_1$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}]$$

Need an expression for [B].

Assume the steady-state approximation for [B].

Obvious here because B is the only intermediate. But essential to include.

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

$$\Rightarrow \quad k_1[\mathrm{A}] = k_2[\mathrm{B}]$$

substitute into $\frac{d[\mathrm{C}]}{dt}$

$$\frac{d[\mathrm{C}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-k_1 t}$$

separate ‘n’ integrate

$$\int_0^{[\mathrm{C}]} d[\mathrm{C}] = k_1[\mathrm{A}]_0 \int_0^{t} e^{-k_1 t}\, dt$$

$$\boxed{[\mathrm{C}] = (1 - e^{-k_1 t})[\mathrm{A}]_0}$$

Much easier than deriving the exact expression for [C] and then applying $k_2 \gg k_1$.

Applying the Steady-State Approximation, cont'd

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad \text{given } k_2 \gg k_1 \qquad \Rightarrow \qquad [C] = (1 - e^{-k_1 t})[A]_0$$

$$\text{looks like } A \xrightarrow{k_1} C$$

So why bother with a mechanism that includes intermediate B?

1. The reaction mechanism must comprise elementary reactions.
   $A \rightarrow C$ is not an elementary reaction.

2. The key to increasing the rate of the reaction $A \rightarrow C$
   is to increase the rate of the reaction $A \rightarrow B$.

Example:

Overall Rxn: $2NO_2Cl \rightarrow 2NO_2 + Cl_2$

Mechanism: $NO_2Cl \rightarrow NO_2 + \bullet Cl$ slow

$NO_2Cl + \bullet Cl \rightarrow NO_2 + Cl_2$ fast

Identifying Reactive Intermediates

1. Must be an intermediate; cannot appear in the overall reaction.

$$\begin{array}{l} A \rightarrow B \\ \underline{B \rightarrow C} \end{array}$$

overall: $A \rightarrow C$

B is an intermediate

$$\begin{array}{l} A \rightarrow 2B + D \\ 2\times \underline{(B \rightarrow C)} \end{array}$$

~~overall: $A \rightarrow B + C + D$~~

overall: $A \rightarrow 2C + D$

B is an intermediate, D is a product

2. Must be reactive. *Use chemical insight.*

inherently unstable: XeF_2 Xe is a noble gas $CH_3O \vdots O\text{-}CH_3$ a peroxide

molecular fragment: •OH •CH_3

an atom: H• Cl• •O•

Example: Reaction Mechanism → Rate Equation.

catalyst

overall reaction: $V^{+3} + Fe^{+3} \xrightarrow{Cu^{+2}} V^{+4} + Fe^{+2}$ in H_2O solution. $\dfrac{d[Fe^{+2}]}{dt} = ?$

Cu in H_2O has two oxidation states: Cu^{+2} (stable) and Cu^{+1} (unstable)

Mechanism of Elementary Reactions:

$$V^{+3} + Cu^{+2} \xrightarrow{k_1} V^{+4} + Cu^{+1}$$

$$Cu^{+1} + Fe^{+3} \xrightarrow{k_2} Cu^{+2} + Fe^{+2}$$

Check – does sum agree with overall reaction? ✓

From reaction 2: $$\frac{d[Fe^{+2}]}{dt} = k_2[Cu^{+1}][Fe^{+3}]$$

Cu^{+1} is a reactive intermediate. $[Cu^{+1}]$ is difficult to measure. Must replace $[Cu^{+1}]$.

Assume the steady-state approximation for Cu^{+1}.

$$\frac{d[Cu^{+1}]}{dt} = 0 = k_1[V^{+3}][Cu^{+2}] - k_2[Cu^{+1}][Fe^{+3}]$$

$$k_1[V^{+3}][Cu^{+2}] = k_2[Cu^{+1}][Fe^{+3}]$$

substitute into expression for $\dfrac{d[Fe^{+2}]}{dt}$

$$\boxed{\frac{d[Fe^{+2}]}{dt} = k_1[V^{+3}][Cu^{+2}]}$$

$$[Cu^{+2}]_0 = [Cu^{+2}] + \cancelto{0}{[Cu^{+1}]}$$

$$[Cu^{+2}]_0 \approx [Cu^{+2}]$$

Example: Rate Equation → Reaction Mechanism

$$\text{overall reaction:}\quad V^{+3} + Fe^{+3} \xrightarrow{Cu^{+2}} V^{+4} + Fe^{+2} \ \text{in } H_2O \text{ solution.}$$

Cu in H_2O has two oxidation states: Cu^{+2} (stable) and Cu^{+1} (unstable)

$$\text{rate equation:}\ \frac{d[Fe^{+2}]}{dt} = k_1[V^{+3}][Cu^{+2}]$$

Clues: V^{+3} and Cu^{+2} are in the rate-limiting step (RLS).

Fe^{+3} is not.

Cu^{+2} can only transform to Cu^{+1}. Cu^{+2} must extract an e^- from something.

Guess first elementary reaction:

$$V^{+3} + Cu^{+2} \rightarrow Cu^{+1} + V^{+4} \qquad \text{rate-limiting step}$$

Next elementary reaction must convert Cu^{+1} to Cu^{+2}.

$$Cu^{+1} + Fe^{+3} \rightarrow Cu^{+2} + Fe^{+2} \qquad \text{fast}$$

Apply steady-state approximation to Cu^{+1}

Note: Clues are not facts.

Another Example: Rate Equation → Reaction Mechanism.

$$2NO + H_2 \rightarrow N_2O + H_2O \qquad \frac{d[N_2O]}{dt} = k[NO][H_2]$$

The only *nitrogen* intermediate is NOH.

Mechanism of Elementary Reactions?

Clues: Overall reaction is ternary; it is unlikely the overall reaction is elementary.

NO and H_2 are in the rate-limiting step.

Guess first elementary reaction:

$$NO + H_2 \xrightarrow{k_1} NOH + H\bullet$$

Must devise reactions for intermediates NOH and H•

$$NOH + NO \xrightarrow{k_2} N_2O + \bullet OH$$

Must devise reaction for intermediate •OH

$$H\bullet + \bullet OH \xrightarrow{k_3} H_2O$$

Another Example: Rate Equation → Reaction Mechanism.

$$2NO + H_2 \rightarrow N_2O + H_2O \qquad \boxed{\frac{d[N_2O]}{dt} = k[NO][H_2]}$$

$$NO + H_2 \xrightarrow{k_1} NOH + H\bullet$$

$$NOH + NO \xrightarrow{k_2} N_2O + \bullet OH$$

$$H\bullet + \bullet OH \xrightarrow{k_3} H_2O$$

Check – does sum agree with overall reaction? ✓

Derive the rate equation. From the second elementary reaction,

$$\frac{d[N_2O]}{dt} = k_2[NOH][NO]$$

Must express [NOH] in terms of abundant species.

Apply the steady-state approximation to NOH.

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

$$k_1[NO][H_2] = k_2[NOH][NO]$$

substitute

$$\boxed{\frac{d[N_2O]}{dt} = k[NO][H_2]}$$ ✓

Another Example: Rate Equation → Reaction Mechanism.

$$2NO + H_2 \rightarrow N_2O + H_2O \qquad \frac{d[N_2O]}{dt} = k[NO][H_2]$$

$$\begin{aligned} NO + H_2 &\xrightarrow{k_1} NOH + H\bullet \\ NOH + NO &\xrightarrow{k_2} N_2O + \bullet OH \\ H\bullet + \bullet OH &\xrightarrow{k_3} H_2O \end{aligned}$$

With steady-state approximation on NOH.

Consider an alternative for the third elementary reaction.

$$\begin{aligned} NO + H_2 &\xrightarrow{k_1} NOH + H\bullet \\ NOH + NO &\xrightarrow{k_2} N_2O + \bullet OH \end{aligned}$$

$$\left.\begin{aligned} NOH + \bullet OH &\xrightarrow{k_3} NO + H_2O \\ NO + H\bullet &\xrightarrow{k_4} NOH \end{aligned}\right\}$$

The sum of these reactions is $H\bullet + \bullet OH \rightarrow H_2O$

The alternative mechanism also agrees with the rate equation.

Apply Occam’s Razor: “As simple as possible, but no simpler.”

William of Occam (1287-1347)