ChemE 2200 – Chemical Kinetics Lecture 5

Today:

Rate Equations from Reaction Mechanisms - Part 1.

"What are the clues of a plausible mechanism of elementary steps?"

Recap:

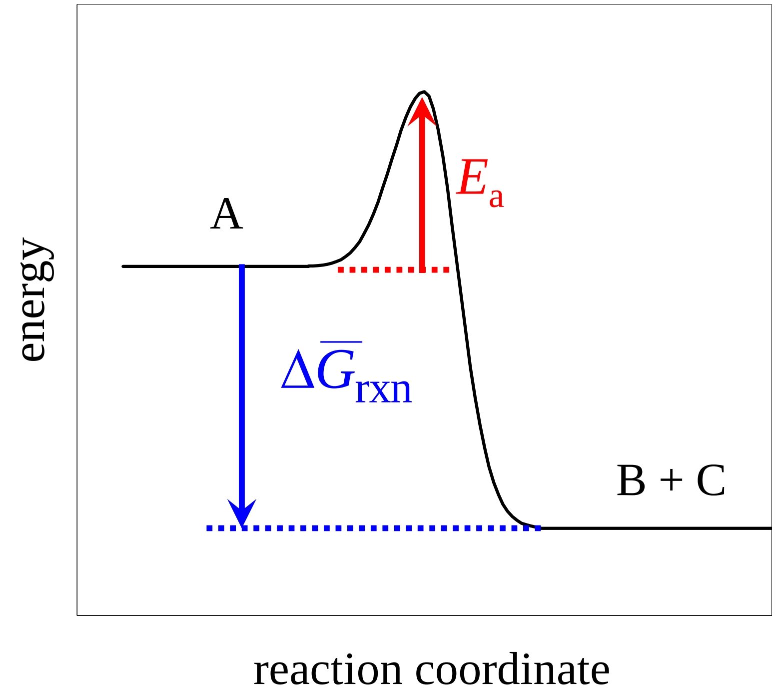
$$A \xrightarrow{k} B + C$$

If reaction is elementary: $$\frac{d[A]}{dt} = -k[A]$$

Arrhenius Theory: $$k = Ae^{-E_a/RT}$$

$A \propto$ rate of reaction attempts

$e^{-E_a/RT} \propto$ fraction of reaction attempts with $E > E_a$



Reading for Kinetics Lecture 6:

McQuarrie & Simon, Chp 29.3-29.4.

Molecular Basis for Rate Equations

Goal: Given an overall reaction $2CO + O_2 \rightarrow CO_2$

and a rate equation $$r_{rxn} = \frac{k_1[CO]^2}{1 + k_2[CO]}$$

Devise the molecular mechanism; devise the sequence of elementary reactions.

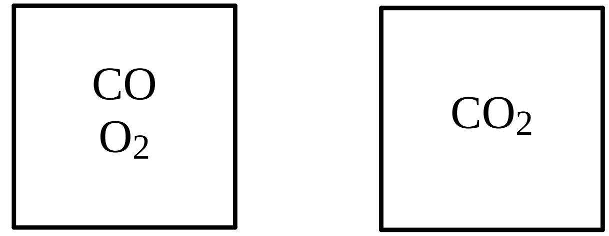
> "A scientist's task of devising a reaction mechanism has been compared with that of a spectator of a drastically shortened version of a classical drama - for example, Hamlet - in which the audience is shown only the opening scenes of the first act and the last scene of the finale. The main characters are introduced, then the curtain falls for a change of scenery, and as it rises again we see on the stage a considerable number of dead bodies and a few survivors. Unraveling what actually happened in between is not an easy task for the inexperienced."

Sture Forsén quoted by Roald Hoffman in "How Should Chemists Think?" *Scientific American*, **268** 66-73 (February 1993).

Molecular Basis for Rate Equations

overall reaction $2CO + O_2 \rightarrow CO_2$

rate equation $r_{\text{rxn}} = \dfrac{k_1[CO]^2}{1 + k_2[CO]}$



before after

Clues: Reaction is not elementary.

Reaction rate $\propto [CO]^2$ at low [CO].

Reaction rate $\propto [CO]^1$ at high [CO].

Reaction rate independent of $[O_2]$.

Elementary reactions?

Intermediates?

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

Our Plan: Gain experience by starting with a mechanism of elementary steps.

Our Plan: reaction mechanism → rate equation

Our Goal: rate equation → reaction mechanism

Devising Elementary Reactions - The Usual Suspects

An elementary reaction must be simple and plausible.

> *"Colonel Mustard in the library with the candle stick."* Simple and plausible.
>
> *"Professor Plum, Ms. Scarlet, and Mr. Green simultaneously and independently assaulted Mr. Body on the grassy knoll."* Not.

Elementary Unimolecular Decomposition: $A \rightarrow \text{products}$ $-\dfrac{d[A]}{dt} = k[A]$

Elementary Bimolecular Reaction: $A + B \rightarrow \text{product(s)}$ $-\dfrac{d[A]}{dt} = k[A][B]$

Elementary Trimolecular Reaction? No.

Infrequent

Improbable correct molecular orientation Consider $2CO + O_2 \rightarrow CO_2$

$$O \equiv C \longrightarrow O = O \longleftarrow C \equiv O$$

$$O = C = O - O = C = O$$

$$\longleftarrow O = C = O \qquad O = C = O \longrightarrow$$

But … "*When you have eliminated all which is impossible, then whatever remains, however improbable, must be the truth.*"

Written for Sherlock Holmes by Sir Arthur Conan Doyle in *The Blanched Soldier.*

Indications of Elementary Reactions

not requirements

neither necessary nor sufficient.

Reaction breaks one bond. $H_2 \rightarrow H\cdot + H\cdot$

$$CH_3CH_2OH \rightarrow CH_3CH_2O\cdot + H\cdot$$

$C \equiv O \rightarrow C + \cdot O\cdot$ a triple bond is one bond.

Reaction makes one bond.

$\cdot O\cdot + C \equiv O \rightarrow O = C = O$ a double bond is one bond.

$H_2C\cdot + \cdot O\cdot \rightarrow H_2C{=}O$ a double bond is one bond.

$CH_2{=}CH_2 + \cdot H \rightarrow \cdot CH_2{-}CH_3$ 0 bonds broken, 1 bond made

Reaction breaks one bond and makes one bond.

$$O{-}N{-}O + C \equiv O \rightarrow O = N + O = C = O$$

Arrhenius Theory - Typical Parameters

Chemical Reaction	Activation Energy, E_a kJ/mol	Activation Energy, E_a eV/molecule	$e^{-E_a/kT}$ 300 K	$e^{-E_a/kT}$ 600 K	A	elementary?	
$O{=}N(O_2)\text{–}O \vdots N(O_2){=}O \rightarrow NO_3 + NO_2$	5	0.05	0.1	0.4 (×4)	10^{15}/sec	yes	breaks 1
$CH_3 \vdots CO\bullet \rightarrow \bullet CH_3 + CO$	43	0.45	3×10^{-8}	2×10^{-4}	10^{15}/sec	yes	breaks 1
$CH_3 \vdots CH_3 \rightarrow \bullet CH_3 + \bullet CH_3$	380	4.0	10^{-66}	10^{-33} ($\times10^{33}$)	10^{17}/sec	yes	breaks 1
$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3\text{–}CH_3$	~0	~0	1	1	10^{11}	yes	makes 1
$NO + O_3 \rightarrow NO_2 + O_2$	11	0.12	0.01	0.1	10^{12}	maybe	breaks 1, makes 1
$NO + Cl_2 \rightarrow NOCl + \bullet Cl$	85	0.89	2×10^{-15}	4×10^{-8}	10^{12}	maybe	breaks 1, makes 1
$2NO_2 \rightarrow 2NO + O_2$	114	1.2	2×10^{-20}	10^{-10}	10^{11}	no	breaks 2, makes 1
$2O_3 \rightarrow 3O_2$	144	1.5	10^{-25}	3×10^{-13}	10^{12}	no	breaks 2, makes 1

$$Cl_2 \rightarrow Cl\bullet + Cl\bullet$$

$$O_3 \rightarrow O_2 + \bullet O\bullet$$

Gaining Experience: First-Order Reactions in Series

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

Elementary Reactions, Batch Reactor with $[\mathrm{B}]_0 = 0$ and $[\mathrm{C}]_0 = 0$

Write the rate equations.

$$\begin{cases} \dfrac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] \\ \dfrac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \\ \dfrac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] \end{cases}$$

substitute

Rate equation for A is a 1st-order decay: $[\mathrm{A}] = [\mathrm{A}]_0 e^{-k_1 t}$

Substitute into the rate equation for B:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-k_1 t} - k_2[\mathrm{B}]$$

cannot be separated

$$\frac{d[\mathrm{B}]}{dt} + k_2[\mathrm{B}] = k_1[\mathrm{A}]_0 e^{-k_1 t}$$

Gaining Experience: First-Order Reactions in Series

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

same terms …

Derive an integrating factor.

$$\mu(t) = \exp\left(\int_0^t k_2\,dt\right) = e^{k_2 t}$$

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

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

$$= e^{k_2 t} k_1[A]_0 e^{-k_1 t}$$

… so substitute

Separate and integrate.

$$\int_{[B]_0=0}^{[B]e^{k_2 t}} d\left([B]e^{k_2 t}\right) = \int_0^t k_1[A]_0 e^{(k_2-k_1)t}\,dt$$

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

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

Gaining Experience: First-Order Reactions in Series

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

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

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

Substitute expressions for [A] and [B] into rate equation for C? $\frac{d[C]}{dt} = k_2[B]$

Easier to use a mass (mol) balance to find [C].

$$[A]_0 + [B]_0 + [C]_0 = [A] + [B] + [C]$$

($[B]_0 \to 0$, $[C]_0 \to 0$)

$$[C] = [A]_0 - [A] - [B]$$

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

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

Check: $t = 0$? ✓

$t \to \infty$? ✓

$k_1 \to \infty$? ✓

$k_2 \to \infty$? ✓

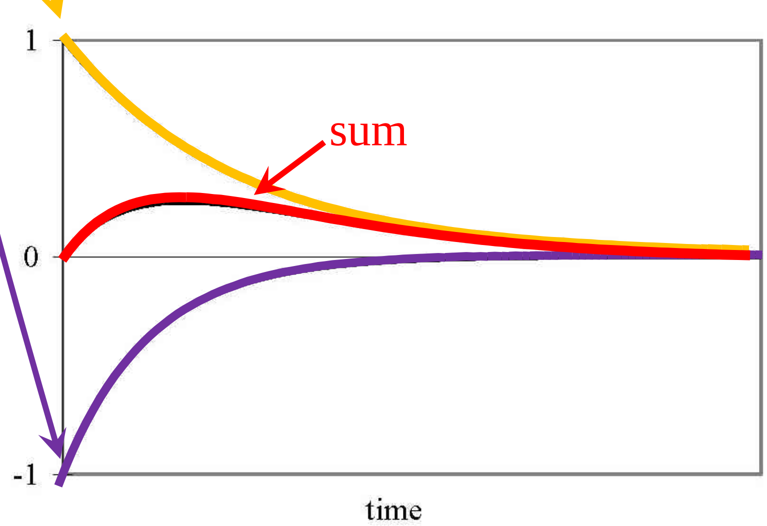
Gaining Experience: First-Order Reactions in Series

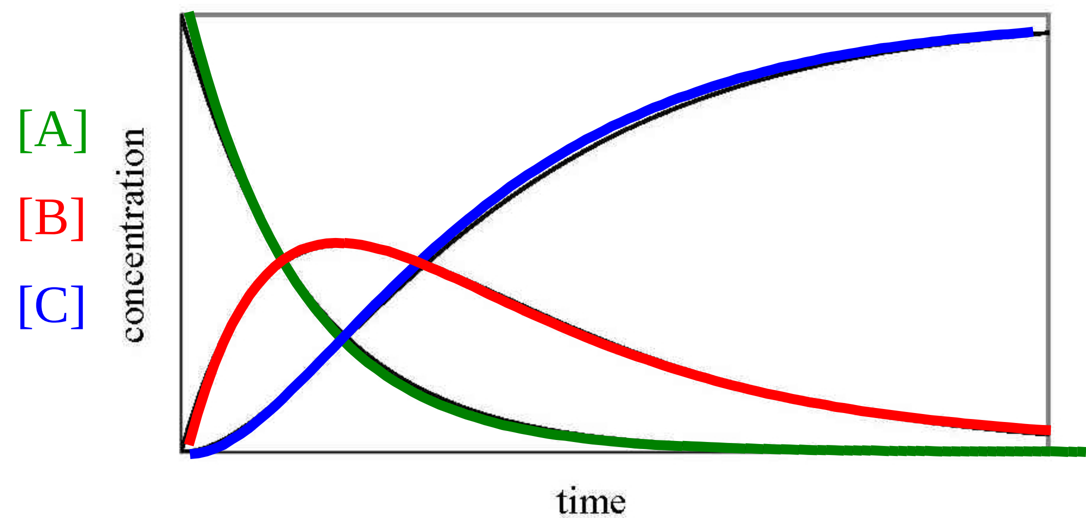
$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

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

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

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

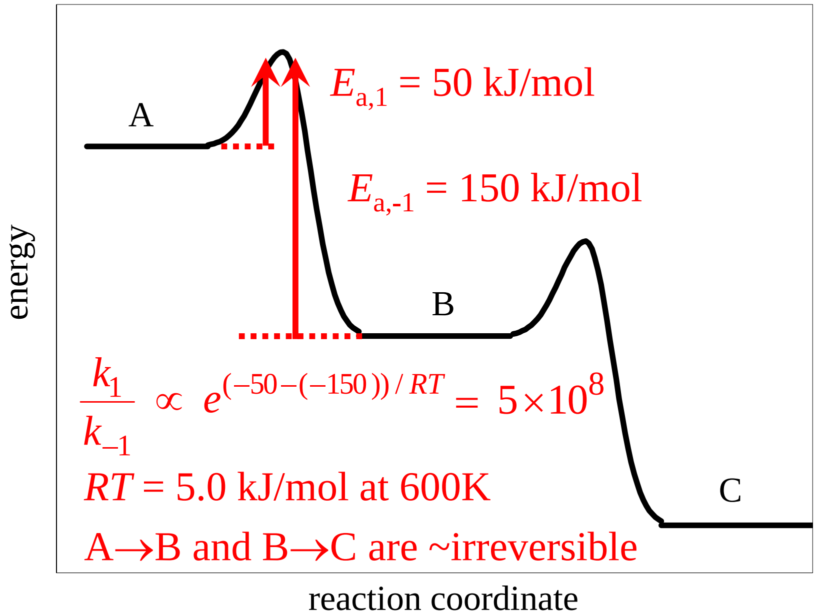


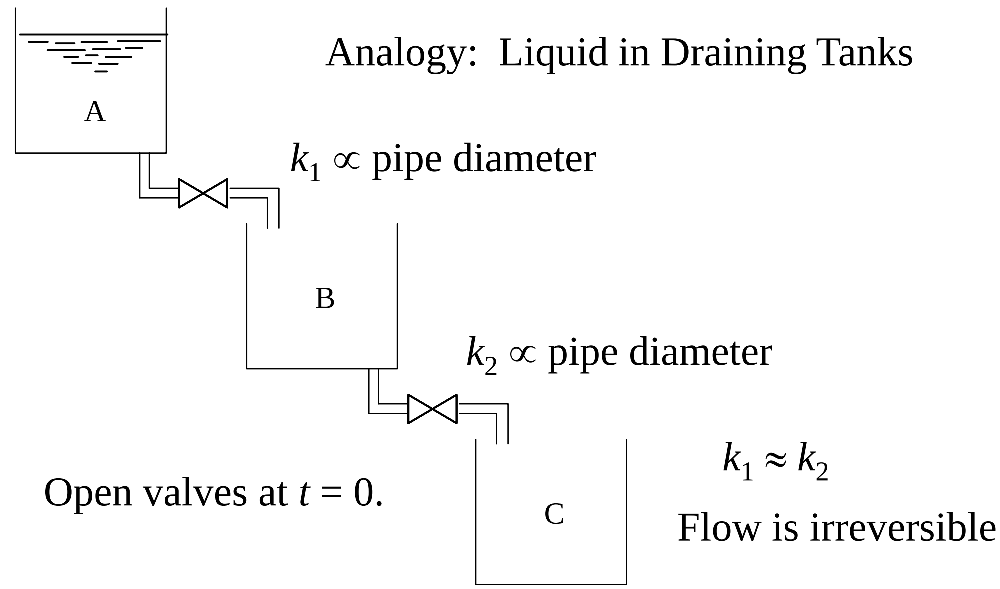


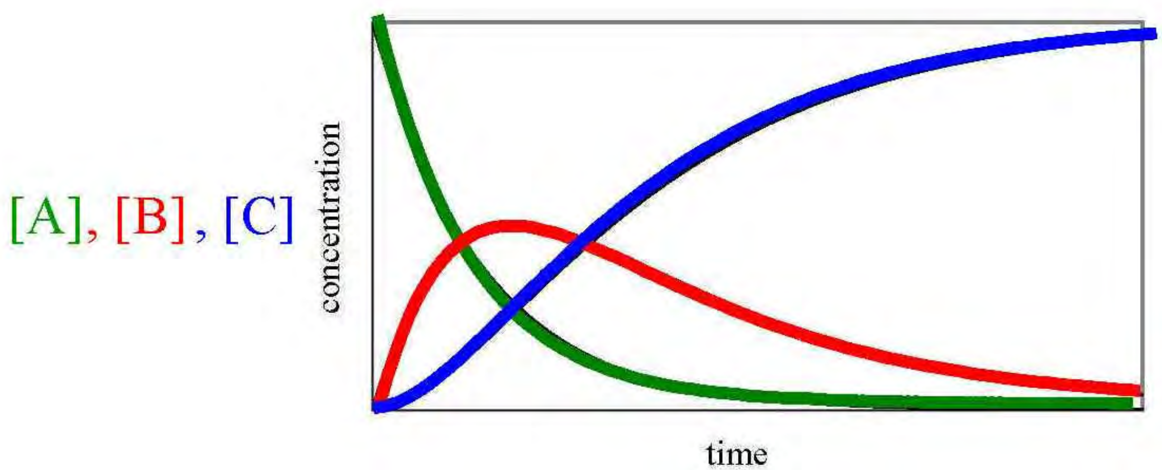
Gaining Experience: First-Order Reactions in Series

overall reaction $\quad A \rightarrow C \quad$ Suppose reaction fails to meet guidelines for an elementary reaction.

Mechanism of elementary reactions: $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ $\quad$ Assume $k_1 \approx k_2$ $\quad$ Effect of intermediate B?





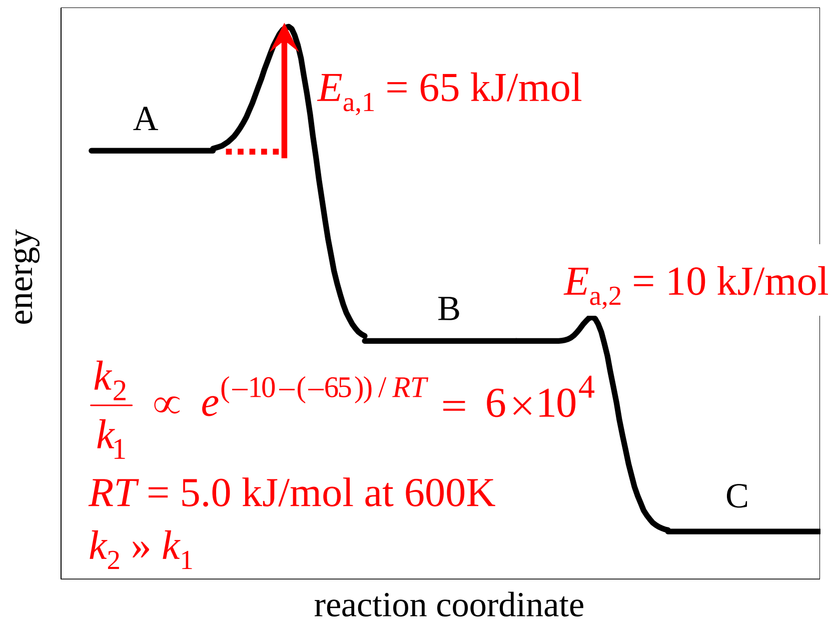


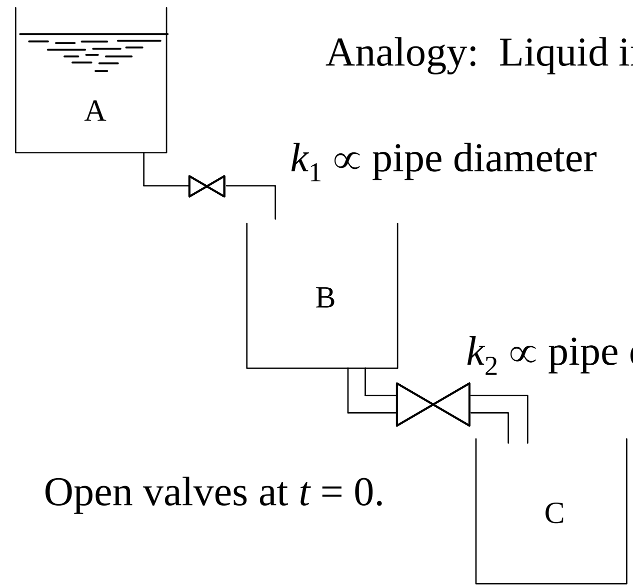
Gaining Experience: First-Order Reactions in Series

overall reaction $A \rightarrow C$

Suppose reaction fails to meet guidelines for an elementary reaction.

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





Analogy: Liquid in Draining Tanks

$k_1 \propto$ pipe diameter

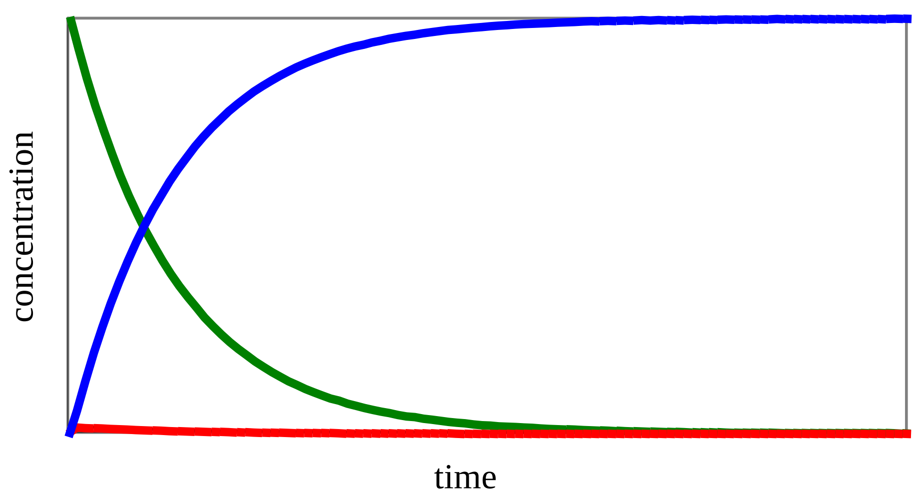
$k_2 \propto$ pipe diameter

Open valves at t = 0.

$k_2 \gg k_1$

Flow is irreversible

[A], [B], [C]



Virtually no accumulation of B.

Reaction appears to be $A \rightarrow C$, but the mechanism requires intermediate B.

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

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

Gaining Experience: First-Order Reactions in Series

overall reaction: $A \rightarrow C$

Suppose reaction fails to meet guidelines for an elementary reaction.

Example:

Overall Rxn: $2NO_2Cl \rightarrow 2NO_2 + Cl_2$ — breaks 2 bonds, makes 1 bond.

Mechanism: $NO_2Cl \rightarrow NO_2 + \bullet Cl$ — breaks 1 bond

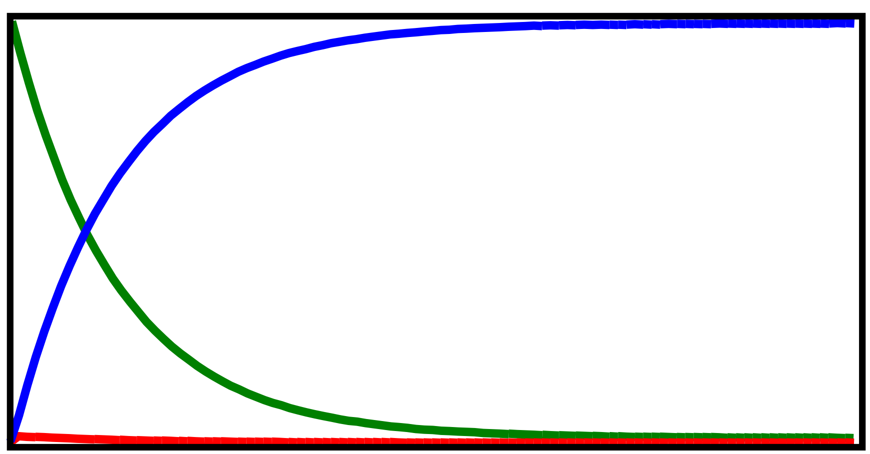
$NO_2Cl + \bullet Cl \rightarrow NO_2 + Cl_2$ — breaks 1 bond, makes 1 bond.

Example:

Overall Rxn: $2O_3 \rightarrow 3O_2$ — breaks 2 bonds, makes 1 bond.

Mechanism: $O_3 \rightarrow O_2 + \bullet O \bullet$ — breaks 1 bond

$O_3 + \bullet O \bullet \rightarrow O_2 + O_2$ — breaks 1 bond, makes 1 bond.



$[O_3]$, $[\bullet O \bullet]$, $[O_2]$