Complex Reactions and Mechanisms (continued)

III) Reversible Reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad\qquad K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

If 1st order, $R_{forward} = R_f = k_1[A]$
$R_{backward} = R_b = k_{-1}[B]$

At Equilibrium, $R_f = R_b \Rightarrow k_1[A]_{eq} = k_{-1}[B]_{eq}$

$$\boxed{K_{eq} = \frac{k_1}{k_{-1}}}$$

a) 1st order reversible reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad\qquad -\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$

$$[B] = [B]_o + ([A]_o - [A])$$

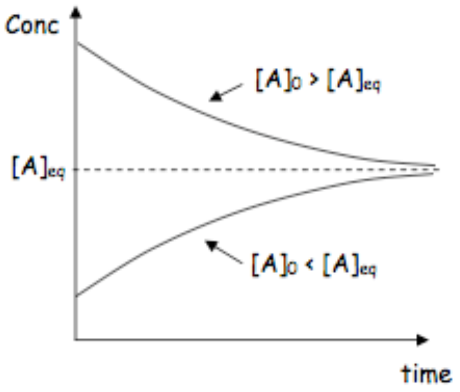
$$\text{So...} \; -\frac{d[A]}{dt} = k_1[A] - k_{-1}([B]_o + [A]_o - [A])$$

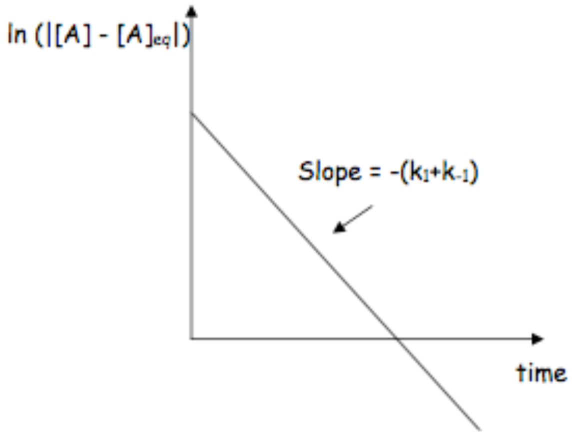
At Equilibrium, $\frac{d[A]}{dt} = 0$

$$\Rightarrow \quad \boxed{[A]_{eq} = \frac{k_{-1}}{k_1 + k_{-1}}\left([B]_o + [A]_o\right)}$$

$$-\frac{d\left([A]-[A]_{eq}\right)}{dt} = -\frac{d([A])}{dt} = (k_1 + k_{-1})\left([A]-[A]_{eq}\right)$$

$$\Rightarrow \quad \boxed{[A]-[A]_{eq} = \left([A]_o - [A]_{eq}\right)e^{-(k_1+k_{-1})t}}$$





<u>Can measure:</u> $K_{eq} = \frac{k_1}{k_{-1}}$ and $k_1 + k_{-1} \equiv k_{obs}$

And extract k_1 <u>and</u> k_{-1}

b) Higher order reactions

e.g. $A + B \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} C$ 2nd order forward, 1st order backward

$$-\frac{d[A]}{dt} = k_2[A][B] - k_{-1}[C] \quad , \quad K = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \quad , \quad K = \frac{k_2}{k_{-1}}$$

After **much** calculation, get… A mess!

We must begin simplifying from the beginning!

Use Flooding in this case: $[B]_o \gg [A]_o,[C]_o$

Then $k_1 \equiv k_2[B]_o \approx k_2[B]$

$$\boxed{-\frac{d[A]}{dt} = k_1[A] - k_{-1}[C]}$$

This is now pseudo 1st order in A

$\Rightarrow$ Looks the same as in part a)

Measure: $K = \frac{k_2}{k_{-1}}$, $k_{obs} \equiv k_1 + k_{-1} = k_2[B]_o + k_{-1}$

By changing $[B]_o$ over a few experiments, can extract k_2 and k_{-1}

IV) Series Reversible Reactions (1st order)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

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

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

Can solve this, but it is an even bigger mess than in part IIIb)!!

And here Flooding, as an approximation, is not going to do much for us.

We need to find new approximations for more complicated mechanisms!

IV) Steady State and Equilibrium Approximations

a) Steady State Approximation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

Assume that [B] is small and **slowly varying**

e.g. $\frac{d[B]}{dt} \approx 0$ and $(k_2 + k_{-1}) \gg k_1$

[B] reaches a steady state concentration $[B]_{SS}$ and remains there

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

Steady State approximation

Solving… $[B]_{SS} = \frac{k_1[A]}{k_{-1} + k_2}$

So $-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]_{SS}$

$$\boxed{-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]}{k_{-1} + k_2}}$$

$$\boxed{\frac{d[C]}{dt} = k_2[B]_{SS} = \frac{k_1 k_2 [A]}{k_{-1} + k_2} = -\frac{d[A]}{dt}}$$

Looks like $A \xrightarrow{k'} C$ (first order) with $k' = \frac{k_1 k_2}{k_{-1} + k_2}$

Necessary Condition for use of Steady State Approximation

- i) Data must be taken <u>after</u> B has built up to a steady state value.
- ii) $(k_2 + k_{-1}) \gg k_1 \Rightarrow [B]_{SS}$ is <u>small</u>

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b) Equilibrium Approximation

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$$

Assume $k_2 \ll k_{-1}$ and k_1

That is... $B \xrightarrow{k_2} C$ is the rate limiting step.

Then... A and B quickly come into equilibrium, while C slowly builds up.

$$K_{eq} = \frac{k_1}{k_{-1}} \underset{\uparrow}{\approx} \frac{[B]}{[A]} \qquad [B] = \frac{k_1}{k_{-1}}[A] = K_{eq}[A]$$

Equilibrium approximation

So... $\frac{d[C]}{dt} = k_2[B] = k_2 K_{eq}[A] = \frac{k_1 k_2}{k_{-1}}[A]$

Or, $$\boxed{\frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}}[A]}$$

Looks like $A \xrightarrow{k'} C$ (first order) with $k' = \frac{k_1 k_2}{k_{-1}}$

In general, for a mechanism with multiple pre-equilibria…

e.g.

$$\begin{array}{lll} A \leftrightarrow I_1 & & K_1 \\ A \leftrightarrow I_2 & & K_2 \\ A \leftrightarrow I_3 & & K_3 \\ A \leftrightarrow I_4 & & K_4 \\ \vdots & & \vdots \\ I_n \leftrightarrow B & & \text{(Rate Determining)} \end{array}$$

$$\boxed{\frac{d[B]}{dt} = k_n[I_n] = k_n\left[\prod_{i=1}^{n} K_i\right][A]}$$

Examples:

A) Apparent Termolecular Reactions (Reaction Chaperones)

$$I + I + M \xrightarrow{k} I_2 + M$$

M is a rare gas molecule or the wall of the reaction vessel

Mechanism:

$$I + I \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} I_2^*$$

$$I_2^* + M \xrightarrow{k_2} I_2 + M^*$$

$$(M^* \longrightarrow M)$$

where $(k_2 + k_{-1}) \gg k_1$, that is the Steady State approximation!

So $$\frac{d[I_2^*]}{dt} = k_1[I]^2 - k_{-1}[I_2^*]_{SS} - k_2[I_2^*]_{SS}[M] \approx 0$$

Steady State approximation

Solving... $$[I_2^*]_{SS} = \frac{k_1[I]^2}{k_{-1} + k_2[M]}$$

And ... $$\boxed{\frac{d[I_2]}{dt} = k_2[I_2^*]_{SS}[M] = k_2[M]\frac{k_1[I]^2}{k_{-1} + k_2[M]}}$$

<u>Limiting Cases</u>

i) $k_2[M] \gg k_{-1}$ then $\frac{d[I_2]}{dt} = k_1[I]^2$

(high pressure) second order

ii) $k_2[M] \ll k_{-1}$ then $\frac{d[I_2]}{dt} = \frac{k_1 k_2}{k_{-1}}[M][I]^2$

(low pressure) third order

B) *Gas decomposition (Lindemann Mechanism)*

$$A(g) \rightarrow \text{products}$$

Mechanism:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^* + M$$

$$A^* \xrightarrow{k_2} \text{products } (B + \ldots)$$

M is a rare gas molecule <u>and/or</u> A,

$\xrightarrow{k_1}$ is fast, $\xleftarrow[k_{-1}]{}$ is very fast, $\xrightarrow{k_2}$ is slow

So… $(k_2 + k_{-1}) \gg k_1$, Steady State approximation again.

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*]_{SS}[M] - k_2[A^*]_{SS} \approx 0$$

Steady State approximation

$$[A^*]_{SS} = \frac{k_1[A][M]}{k_{-1}[M]+k_2}$$

$$\boxed{-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_2[A^*]_{SS} = \frac{k_1k_2[A][M]}{k_{-1}[M]+k_2}}$$

Limiting Cases

i) High pressure (1 bar) $k_{-1}[M] \gg k_2$

$$-\frac{d[A]}{dt} = \frac{k_1k_2}{k_{-1}}[A] = k_\infty[A] \qquad (1^{st}\text{ order})$$

ii) Low pressure ($\sim 10^{-4}$ bar) $k_{-1}[M] \ll k_2$

$$-\frac{d[A]}{dt} = k_1[A][M] \qquad (\text{if } M \equiv A\text{, then } 2^{nd}\text{ order in } A)$$