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

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

a) 1st order reversible reactions

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

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

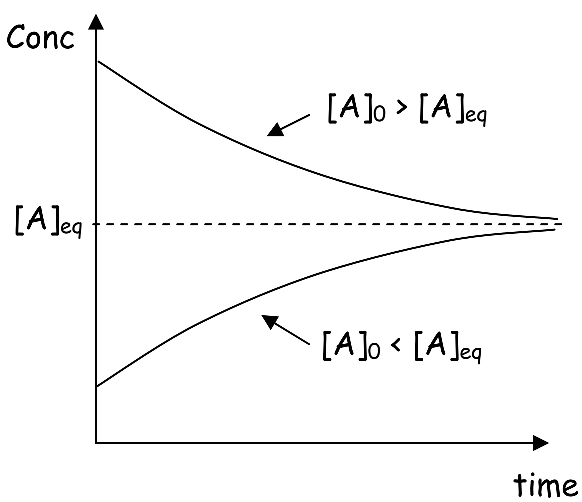
So… $-\dfrac{d[A]}{dt} = k_1[A] - k_{-1}\left([B]_o + [A]_o - [A]\right)$

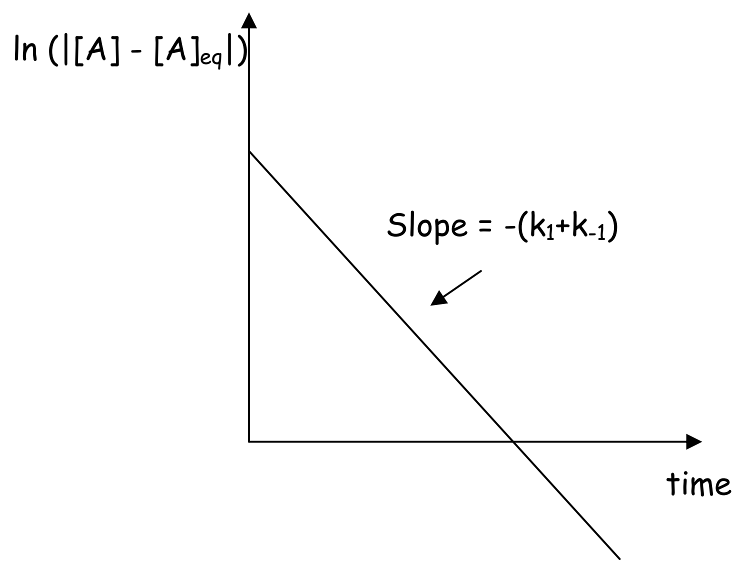
At Equilibrium, $\frac{d[A]}{dt} = 0$

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

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

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





<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. $A + B \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} C$ 2^{nd} order forward, 1^{st} 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 1^{st} 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) <u>Series Reversible Reactions (1st order)</u>

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

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

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

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!