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5.60 Thermodynamics & Kinetics  
Spring 2008

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## Complex Reactions and Mechanisms (continued)

### III) Reversible Reactions

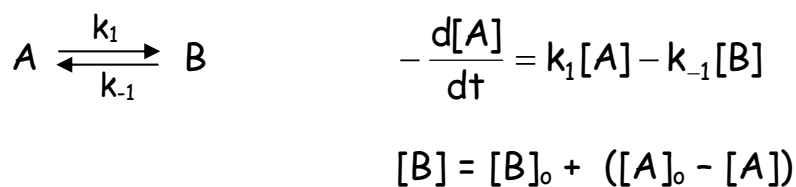


If 1<sup>st</sup> order,  $R_{forward} = R_f = k_1[A]$   
 $R_{backward} = R_b = k_{-1}[B]$

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

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

a) 1<sup>st</sup> order reversible reactions



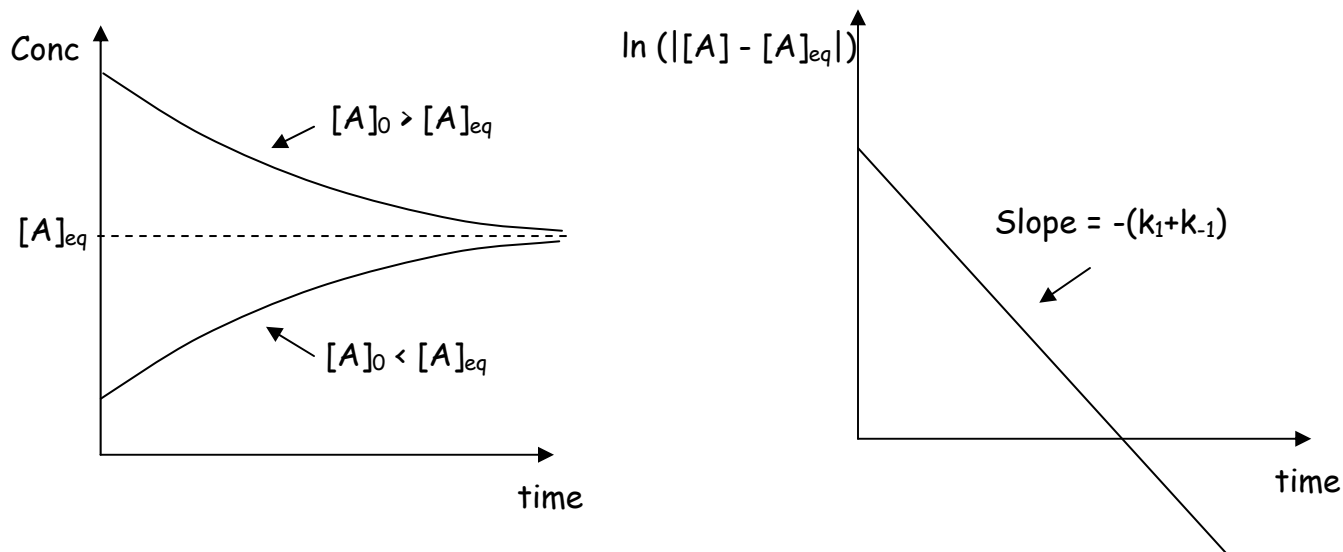
So...  $-\frac{d[A]}{dt} = k_1[A] - k_{-1}([B]_0 + [A]_0 - [A])$

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

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

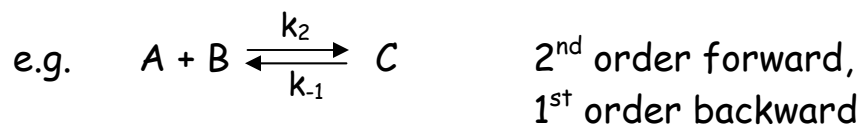
$$-\frac{d([A] - [A]_{eq})}{dt} = -\frac{d([A])}{dt} = (k_1 + k_{-1})([A] - [A]_{eq})$$

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



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

And extract  $k_1$  and  $k_{-1}$

b) Higher order reactions

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

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

We must begin simplifying from the beginning!

Use Flooding in this case:  $[B]_0 \gg [A]_0, [C]_0$

Then  $k_1 \equiv k_2[B]_0 \approx k_2[B]$

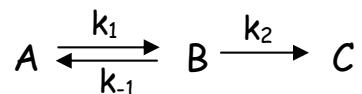
$$\boxed{-\frac{d[A]}{dt} = k_1[A] - k_{-1}[C]}$$

This is now pseudo 1<sup>st</sup> order in A

⇒ Looks the same as in part a)

Measure:  $K = \frac{k_2}{k_{-1}}, \quad k_{obs} \equiv k_1 + k_{-1} = k_2[B]_0 + k_{-1}$

By changing  $[B]_0$  over a few experiments, can extract  $k_2$  and  $k_{-1}$

**IV) Series Reversible Reactions (1<sup>st</sup> order)**

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

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

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

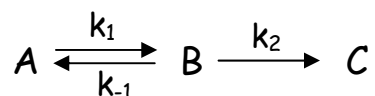
Can solve this, but it is an even bigger mess than in part IIIb)!!

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



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

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

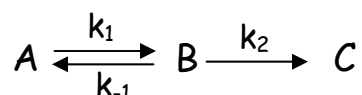
$$\boxed{\frac{d[C]}{dt} = k_2 [B]_{SS} = \frac{k_1 k_2 [A]}{k_{-1} + k_2} = -\frac{d[A]}{dt}}$$

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 after B has built up to a steady state value.
- ii)  $(k_2 + k_{-1}) \gg k_1 \Rightarrow [B]_{ss}$  is small

b) Equilibrium Approximation



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.

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

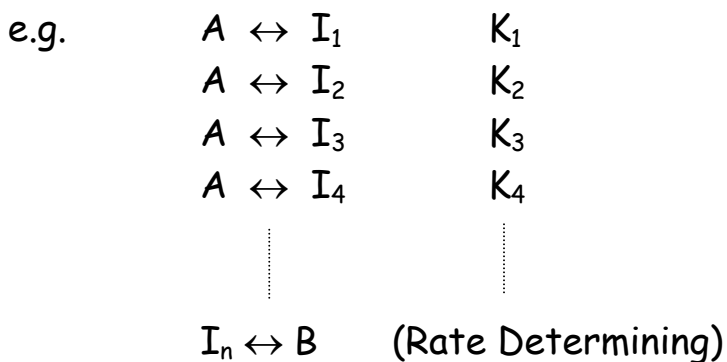
Equilibrium approximation

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

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

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...

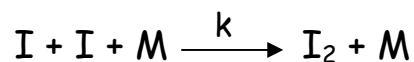


$$\frac{d[B]}{dt} = k_n [I_n] = k_n \left[ \prod_{i=1}^n K_i \right] [A]$$

### Examples:

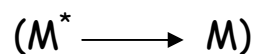
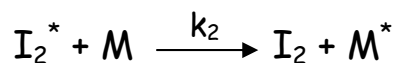
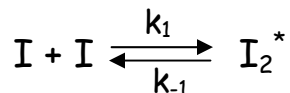
A) Apparent Termolecular Reactions (Reaction Chaperones)





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

Mechanism:



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

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

Steady State approximation

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

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

Limiting Cases

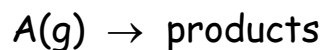
$$\text{i) } k_2[M] \gg k_{-1} \quad \text{then} \quad \frac{d[I_2]}{dt} = k_1[I]^2$$

(high pressure) second order

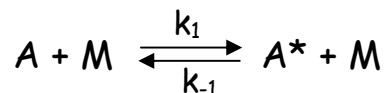
$$\text{ii) } k_2[M] \ll k_{-1} \quad \text{then} \quad \frac{d[I_2]}{dt} = \frac{k_1 k_2}{k_{-1}} [M][I]^2$$

(low pressure) third order

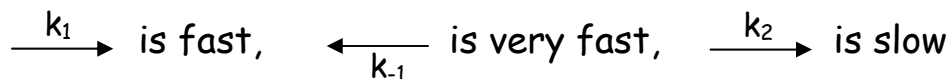
### B) Gas decomposition (Lindemann Mechanism)



Mechanism:



M is a rare gas molecule and/or A,



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)       $k_{-1}[M] \gg k_2$

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

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

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