Lecture 15: Kinetics (continued)

Announcements:

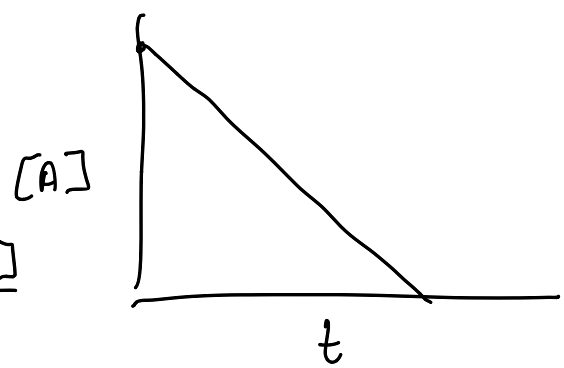
- Tomorrow: Dr. Nikki Goodwin (GSK)
    - CBI Seminar (FOR STUDENTS!). Pizza at 11:30. Talk starting about noon. 219 BRL
    - Research Seminar: 4pm, 101 BRL

Today:

- Kinetics...

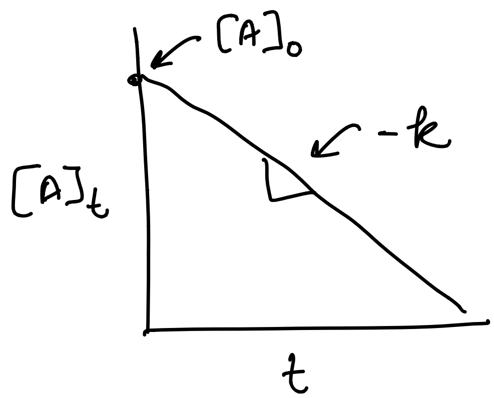
$A \longrightarrow P$

$\emptyset$-order in $[A]$



$$\text{rate} = k = -\frac{d[A]}{dt}$$

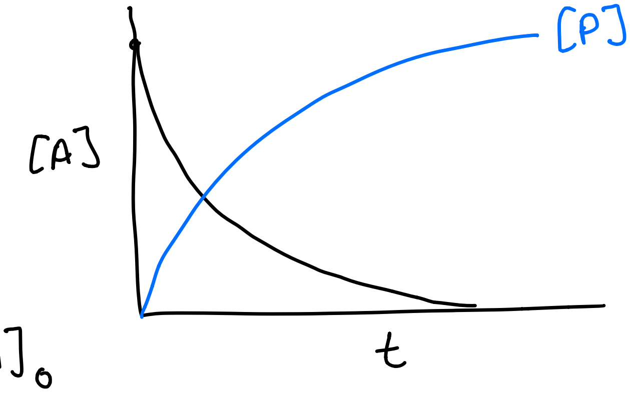
$$[A]_t - [A]_0 = -kt \rightarrow [A]_t = -kt + [A]_0$$

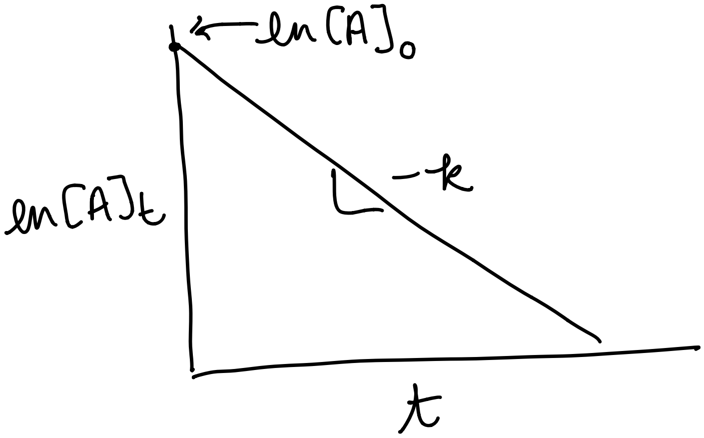


1st Order in [A]

rate = k [A]

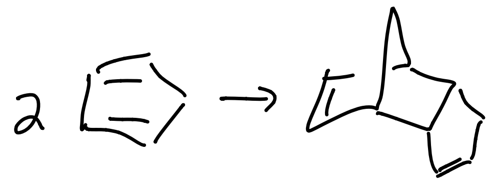
$$\ln[A]_t = -kt + \ln[A]_0$$

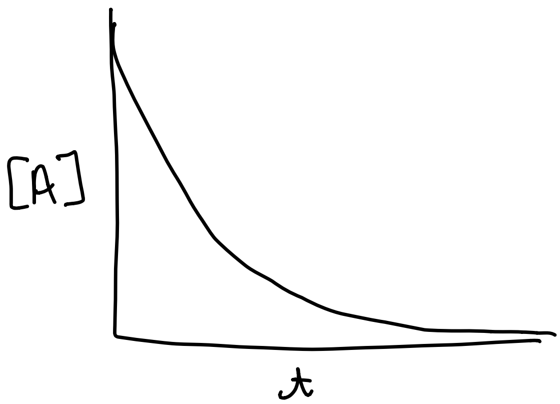




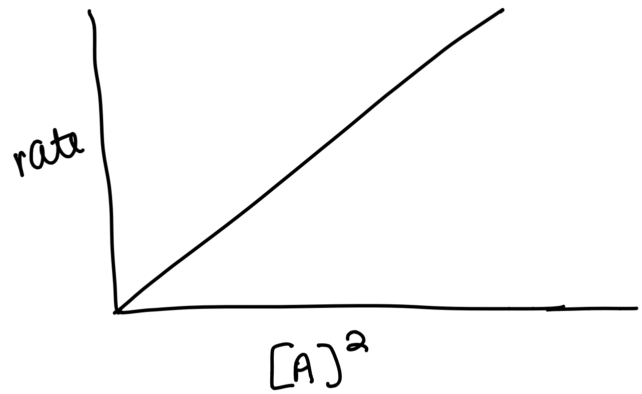
2nd Order Kinetics

Situation 1: $A + A \xrightarrow{k} P$





$$\text{rate} = k[A]^2$$



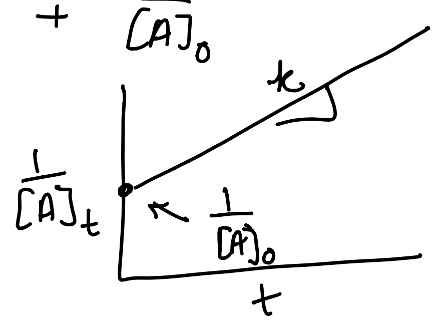
Integrated Rate Law:

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^2$$

$$\int_0^t \frac{1}{[A]^2}\, d[A] = \int_0^t -k\, dt$$

$$+\frac{1}{[A]_t} + \frac{-1}{[A]_0} = +kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$



So.... for $A \rightarrow P$

① Measure $[A]$ vs. time

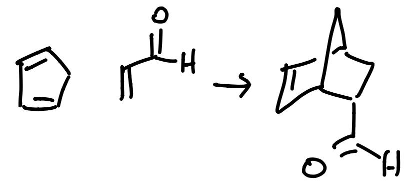
② Plot $[A]_t$ vs. time $\rightarrow$ $\emptyset$ order in $[A]$

$\ln[A]_t$ vs. time $\rightarrow$ 1st order

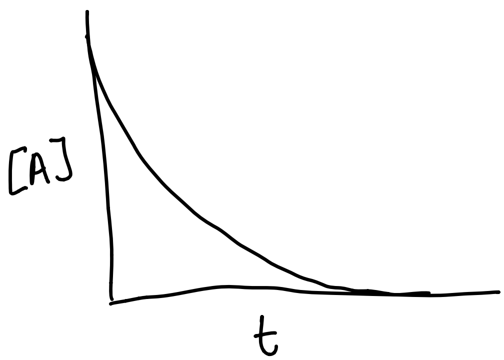
$\frac{1}{[A]_t}$ vs. time $\rightarrow$ 2nd order

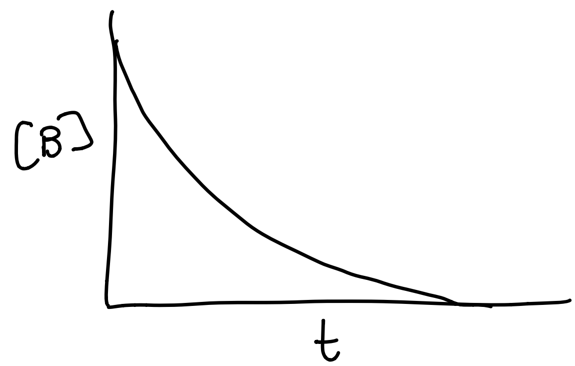
③ Which has best fit? (Highest R^2)

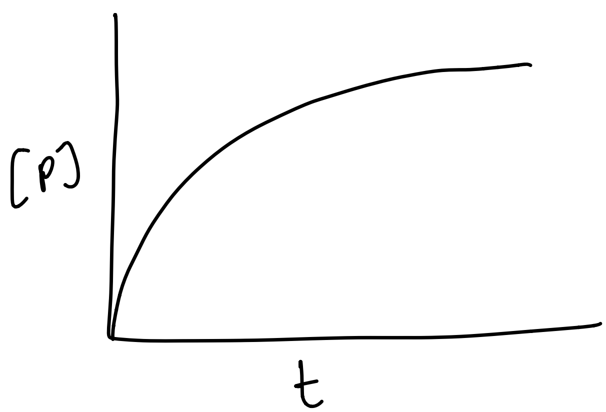
2^{nd} Order: Situation 2



$$A + B \longrightarrow P$$







If $[B]_0 = [A]_0$, then $[B]_t = [A]_t$ &

rate $= k[A]^2$ ← unusual

if $[B]_0 \neq [A]_0$ (more B than A)

$$[B]_t = [B]_0 - ([A]_0 - [A]_t)$$

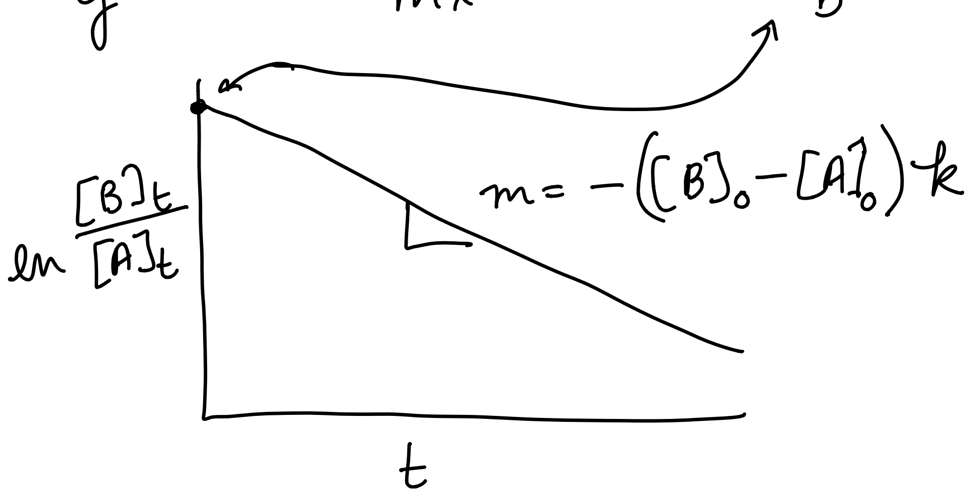
$$\text{rate} = -\frac{d[A]}{dt} = \left(-\frac{d[B]}{dt} = \frac{d[P]}{dt}\right) = k[A][B]$$

$$-\frac{d[A]}{dt} = k[A]\left([B]_0 - ([A]_0 - [A]_t)\right)$$

$$\int_0^t \frac{d[A]}{[A]\left([B]_0 - ([A]_0 - [A]_t)\right)} = \int_0^t -k\,dt$$

$$\frac{1}{([B]_0 - [A]_0)} \ln\frac{[B]_t}{[A]_t} - \frac{1}{([B]_0 - [A]_0)} \ln\frac{[B]_0}{[A]_0} = -kt$$

$$\underbrace{\ln\frac{[B]_t}{[A]_t}}_{y} = \underbrace{-([B]_0 - [A]_0)kt}_{mx} - \underbrace{\frac{1}{([B]_0 - [A]_0)} \ln\frac{[B]_0}{[A]_0}}_{b}$$



Simplification: Pseudo-1st Order Kinetics

→ Use lots of B (≥ 10 equiv)

→ $[B]_t \approx [B]_0$

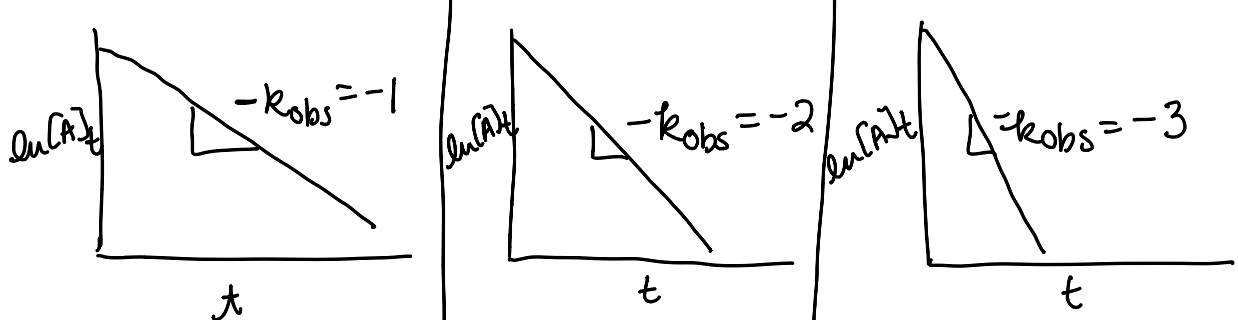
$$\text{rate} = k[A][B] \approx k[A]\underbrace{[B]_0}_{\text{constant}}$$

$$\text{rate} = k_{obs}[A] = \underbrace{\left(k[B]_0\right)}_{\text{constant}}[A]$$

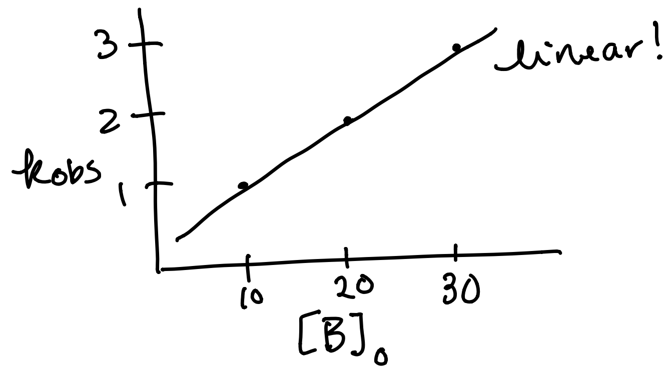
Now use 1st order treatment...

$[A]_0 = 1\text{ mM}$

$[B]_0 = 10\text{ mM}$ | $[B]_0 = 20\text{ mM}$ | $[B]_0 = 30\text{ mM}$



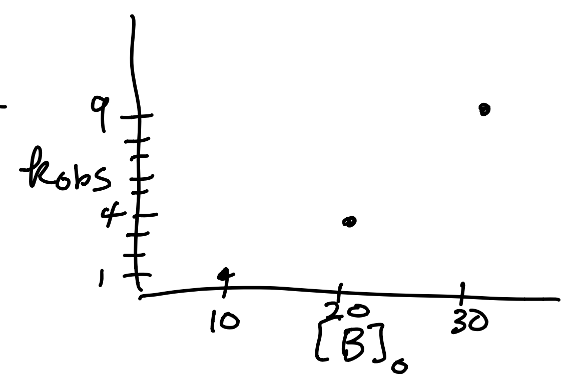
$[B]_0$ (mM)	k_{obs}
10	1
20	2
30	3



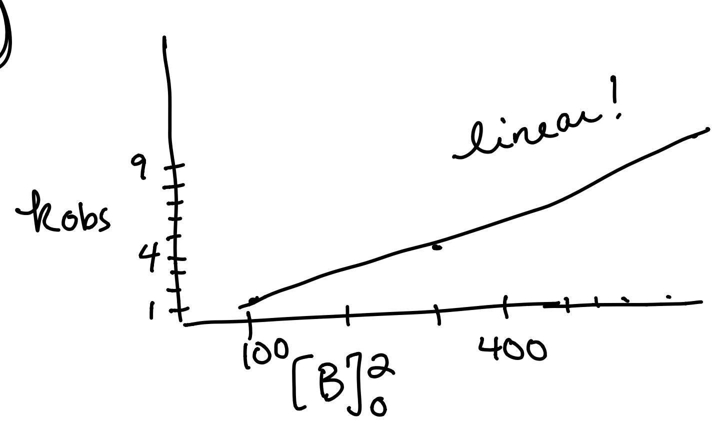
$$\text{rate} = k_{obs}[A] = k[A][B]$$

1st order ✓ 1st order ✓

$[B]_0$ (mM)	k_{obs}
10	1
20	4
30	9



$$k_{obs} = k[B]_0^{x}$$



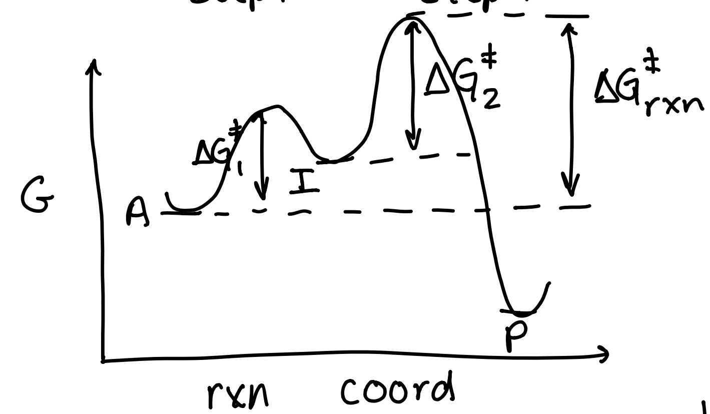
2^{nd} order in $[B]$!

$\boxed{\text{See what fits}}$

Multi-Step Reactions

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P$$

Step 1   Step 2



$$\text{rate} = \frac{d[P]}{dt} = k_2[I]$$

hard to measure [I] in this case.

If [I] does not change: Steady-State Approximation

$$\frac{d[I]}{dt} = \varnothing = k_1[A] - k_{-1}[I] - k_2[\cancel{P}]$$

$$k_1[A] = k_{-1}[I] + k_2[I]$$

$$\frac{k_1[A]}{k_{-1}+k_2} = [I]$$

$$\text{rate} = \frac{k_2 k_1 [A]}{k_{-1}+k_2}$$

} everything that makes P

} everything that destroys I.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P$$

Step 1