

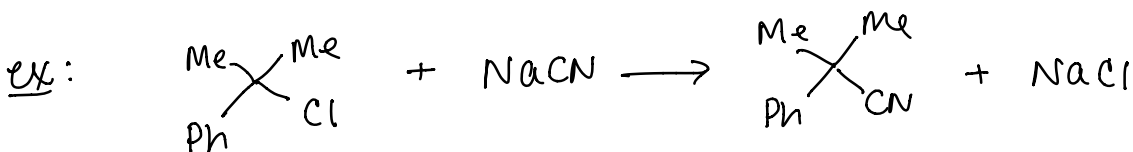
Lecture 16: Kinetics (continued)

Announcements:

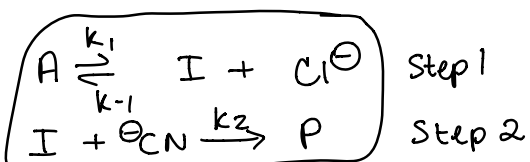
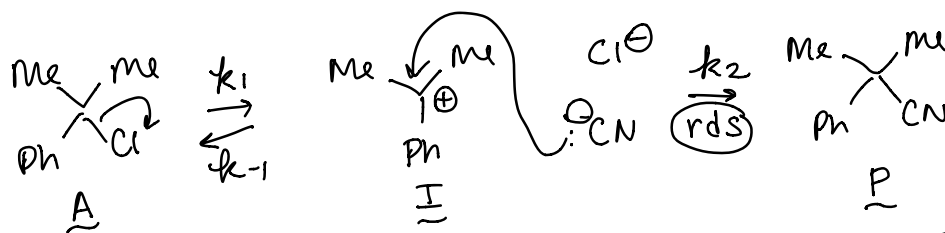
- Problem Set 4 due Thurs, Nov 3 (will be posted today)
- Organic Journal Club today at 12:30
- For transition metal catalysis: See Grossman's *The Art of Writing Reasonable Organic Reaction Mechanisms*, Chapter 6

Today:

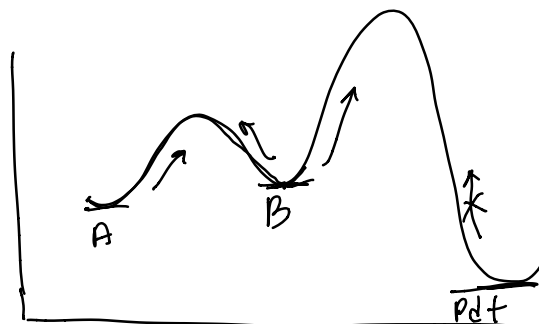
- More on the steady state approximation
- Saturation kinetics
- Equilibrium approximation
- How we actually determine rate laws experimentally
- Radical reactions



Hypothesis: $\text{S}_{\text{N}}1$



If Step 1 = rds: $\text{rate} = k_1 [\text{A}]$



If Step 2 = rds:
$$\text{rate} = \frac{k_1 [A] k_2 [\text{I}^-] [\text{CN}^-]}{k_{-1} [\text{I}^-] [\text{Cl}^-] + k_2 [\text{CN}^-]}$$

$$\text{rate} = k_2 [\text{I}^-] [\text{CN}^-]$$

SSA:
$$\frac{d[\text{I}^-]}{dt} \approx 0 = k_1 [A] - k_{-1} [\text{I}^-] [\text{Cl}^-] - k_2 [\text{I}^-] [\text{CN}^-]$$

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

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

Reverse Step 1 is much faster than Step 2.

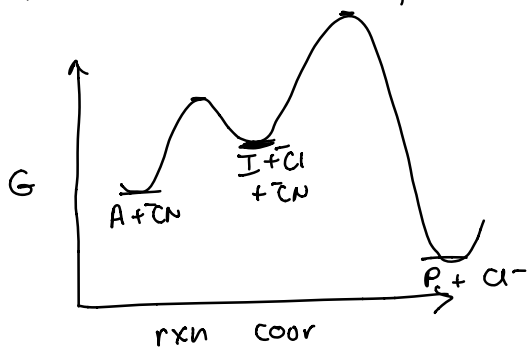
rate dependence on $[\text{CN}^-]$

Limiting Cases:

① If $k_{-1} [\text{Cl}^-] \gg k_2 [\text{CN}^-]$,
$$\text{rate} = \frac{k_1 k_2 [A] [\text{CN}^-]}{k_{-1} [\text{Cl}^-]}$$

1st step is reversible

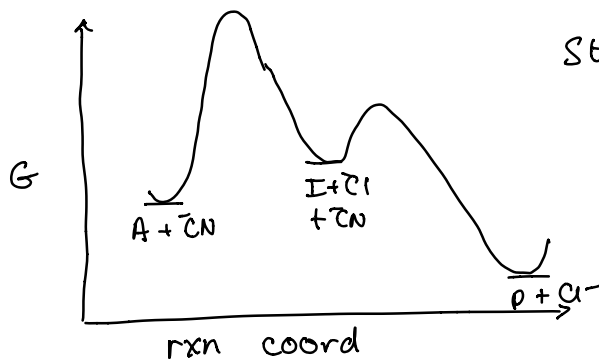
2nd Step = rds

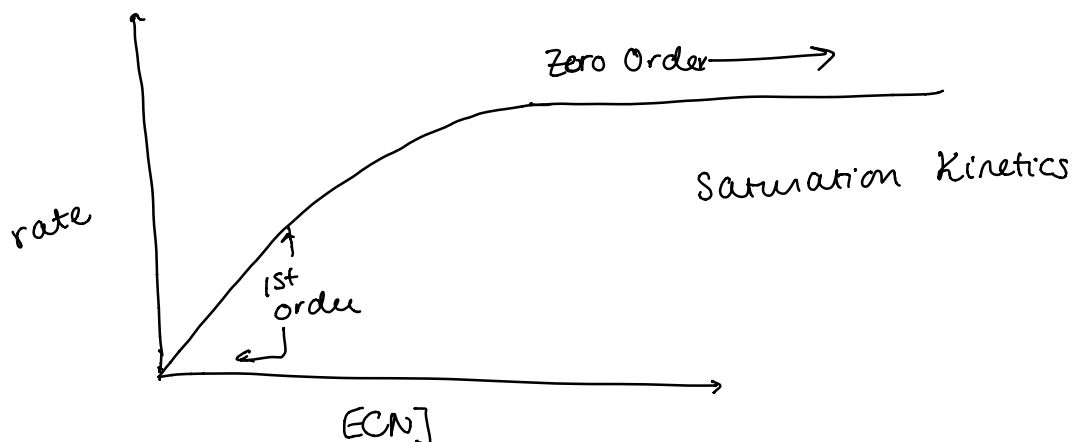


② If $k_2 [\text{CN}^-] \gg k_{-1} [\text{Cl}^-]$,

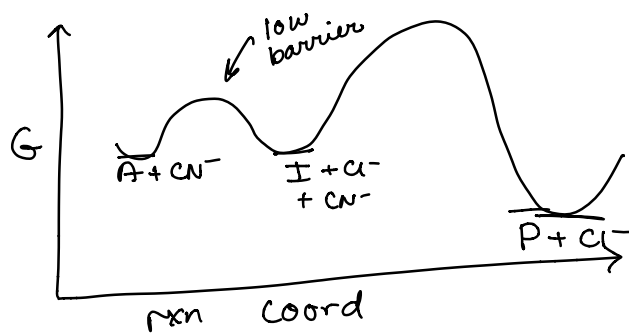
$$\text{rate} = \frac{k_1 k_2 [A] [\text{CN}^-]}{k_2 [\text{CN}^-]} = k_1 [A]$$

Step 1 = rds





What if $[I^-]$ does change or build-up?



$[I^-]/K \rightarrow$ not true for S_N1

Use equilibrium approximation:

$$K_{eq} = \frac{[I^-][CN^-]}{[A]} \Rightarrow [I^-] = \frac{K_{eq}[A]}{[CN^-]} = \frac{k_1}{k_{-1}} \frac{[A]}{[CN^-]}$$

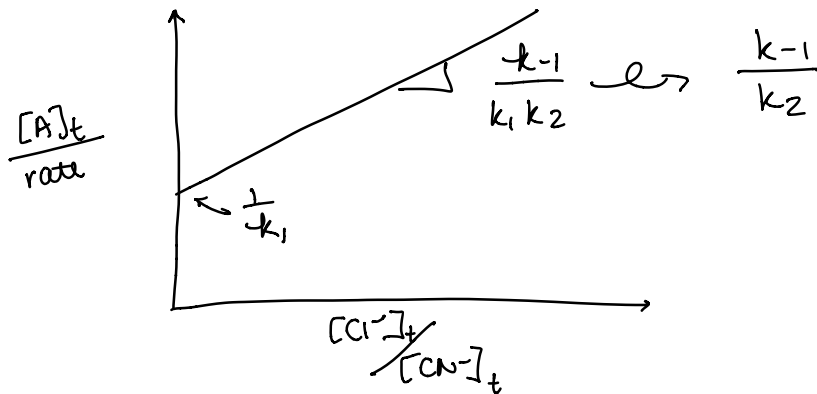
$$\text{rate} = k_2 [I^-][A] = k_2 \frac{k_1 [A] [A] [CN^-]}{k_{-1} [CN^-]}$$

What about non-limiting cases? How do plot data in a meaningful way?

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

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

$$\frac{[A]_t}{\text{rate}} = \frac{k_{-1}}{k_1 k_2} \left(\frac{[\text{Cl}^-]}{[\text{CN}^-]} \right) + \frac{1}{k_1} \quad y = mx + b$$



How do experimentally determine rate laws?

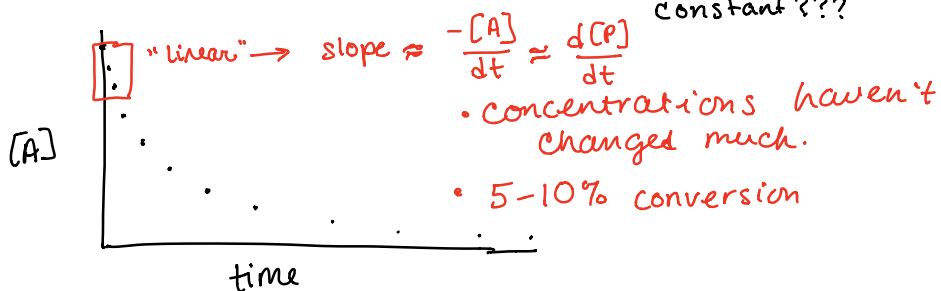
Options:

① Initial Rates



$$\text{rate} = \frac{d[P]}{dt} = k_{\text{obs}} [A]^m [B]^n [C]^o$$

constant???



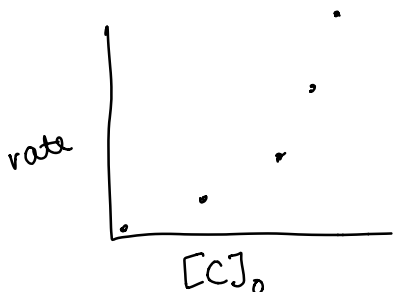
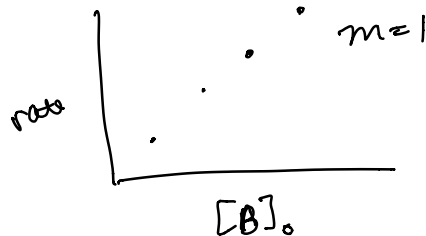
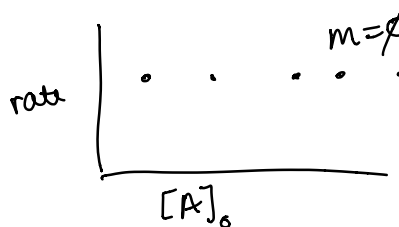
Pros: Fast, easy, rate

Cons: • Error is inherent

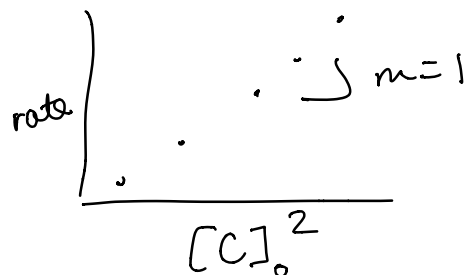
• Concentrations are changing (& it might matter).

• First 10% may not be representative (Induction Period)

If "clean" behavior → So USEFUL!



↪



② Full Kinetic Profile

Con: rate constants may be complicated

Pro: information about whole rxn course.

How to deal w/ nonlinear data:

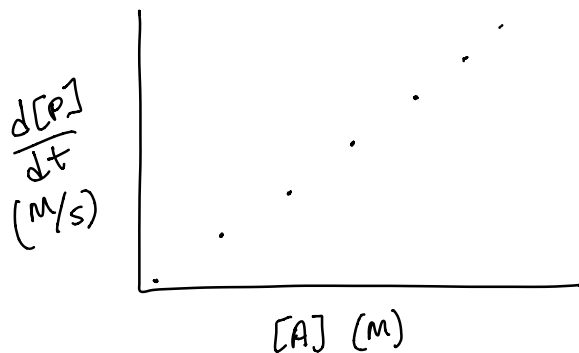
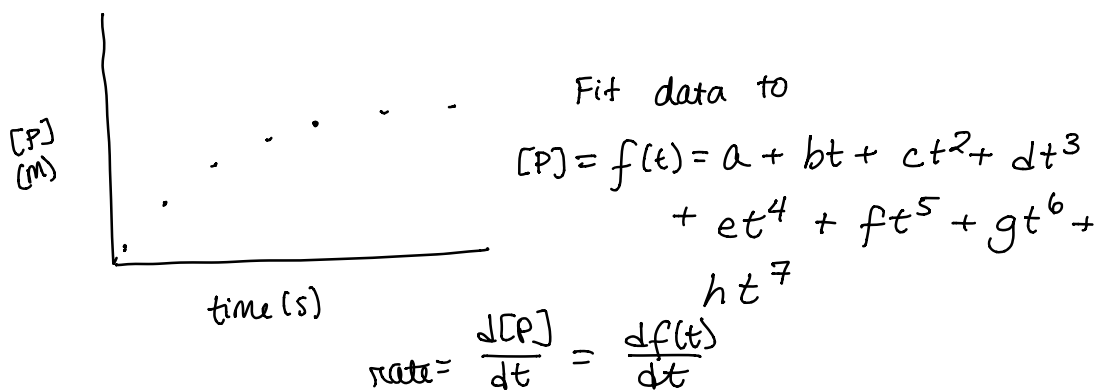
Ø) → Integrated rate laws

1) Nonlinear fitting (nonlinear regression program to fit to an appropriate equation)

Programs: Kinsim, Kaleidograph

2) Extract rates using math & Excel

ex: JACS 2007, 129, 1587a



Collecting Data : Options

① Take aliquots : Easy

under "normal" conditions

Does taking aliquots change rxn?

Relatively few data points

② In situ monitoring of concentrations or rates

NMR
IR
UV/Vis

Rxn Calorimetry
measuring heat flow.

Donna Blackmond