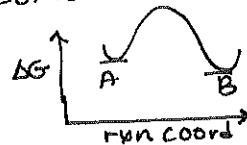


# ① LECTURE 11: RATE EQUATIONS

PS#5 due Tues 10/13

## ② (ELEMENTARY STEP)

Last time:  
1-step rxn:  
 $A \rightarrow B$



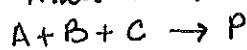
$$\text{rate} = k[A]$$

Knowing rate  $\rightarrow$  knowing  $\Delta G^\ddagger$  (Eyring Eqn)

We can also determine

COMPOSITION of T.S. relative to G.S.

Important tool in understanding multi-component +/or multi-step rxns.



$$\text{rate} = k[A]^m[B]^n[C]^p$$

③ Exponents (m, n, p)  $\rightarrow$  Composition relative to g.s.

ex:

$$\text{rate} = k[A]^1$$

Same number of A molecules in G.S. & TS.

G.S.	TS
1 molecule	1 molecule
2 molecules	2 molecules
10 molecules	10 molecules
etc.	

④ ex:

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

Twice as many A's in T.S. as G.S.

ex:

$$\text{rate} = k[A]^{1/2}$$

Half as many A's in TS as GS

ex:

$$\text{rate} = k[A]^1[B]^1$$

Equal number of A's & B's in TS

Same number of A's in TS as GS & of B's in TS as GS.

## ⑤ Multistep Rxns

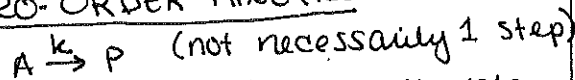
Remember: Only elementary steps that occur before or during the rate-determining step can be detected.

In practice...

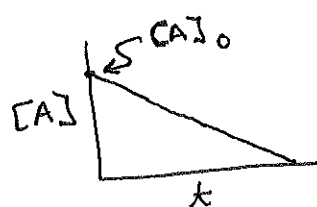
You propose >1 mechanism & see if you can use kinetics to distinguish them / rule 1 out.

So... we need to be able to write rate laws for our proposed mechanisms.

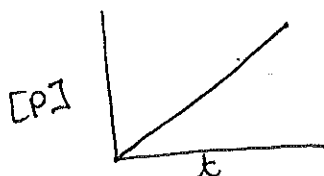
## ⑥ ZERO-ORDER KINETICS



$$\text{rate} = -\frac{d[A]}{dt} = \frac{d[P]}{dt} = k \quad \text{NO rate dependence on } [A].$$



rate law



Linear decay of A.  
Linear growth of P.

⑦ can also write an integrated Rate Law (OLD SCHOOL, BUT MAKES LINEAR PLOTS, SO SATISFYING)

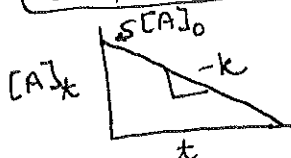
$$-\frac{d[A]}{dt} = -k$$

$$d[A] = -k dt$$

$$\int_0^t d[A] = \int_0^t -k dt$$

$$\boxed{[A]_t - [A]_0 = -kt}$$

Integrated Rate Law



⑧ First-Order Kinetics ≡ 1<sup>st</sup> order rate dependence on [A]



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



NOT LINEAR!

Rxns "slow down" as you near completion.

⑨ Integrated Rate Law

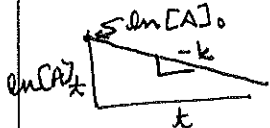
$$-\frac{d[A]}{dt} = k[A]$$

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

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

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

$$\ln [A]_t = -kt + \underbrace{\ln [A]_0}_{\text{you know this.}}$$



⑩ How long do rxns take to get to 50% SM & 50% P?

$$[A]_t = \frac{1}{2} [A]_0$$

$$[A]_0 = 2 [A]_t$$

$$\ln [A]_t - \ln 2 [A]_t = -kt$$

$$\ln \frac{[A]_t}{2[A]_t} = -kt$$

$$\ln \frac{1}{2} = -kt$$

$$\underbrace{\ln 1}_{=0} - \ln 2 = -kt$$

$$\ln 2 = kt$$

$$t_{1/2} = \frac{\ln 2}{k}$$

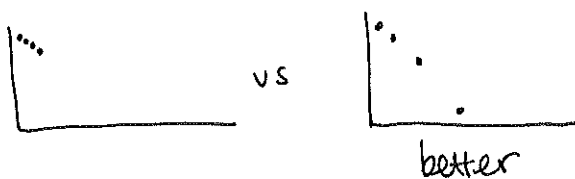
Does not depend on [A] or [A]₀!

⑪ Practical Considerations

- ln x plots tend to look linear  
→ Measure [A] over 3-5 half-lives.

- How many data points?  
As many as possible.  
≥ 10-20.

Spread out over entire range:



⑫ Why half-life should matter to every synthetic chemist...

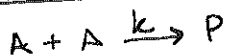
$t_{1/2}$	time (h)	% yield
1	2	50
2	4	75
3	6	87.5
4	8	93.75
5	10	96.875

\* If you get 50% yield after 2 hours, a 1<sup>st</sup>-order rxn will not give 100%.

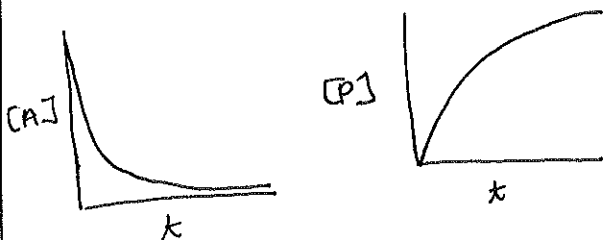
WORSE FOR HIGHER-ORDER RXNS.

13 SECOND-ORDER KINETICS

Situation #1



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



14 Integrated Rate Law

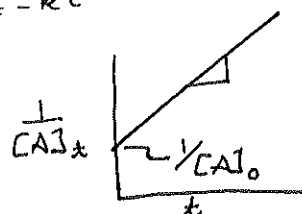
$$-\frac{d[A]}{dt} = k[A]^2$$

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

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

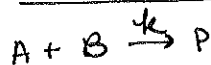
$$-\frac{1}{A_x} - \left(-\frac{1}{A_0}\right) = -kt$$

$$\frac{1}{A_x} - \frac{1}{A_0} = kt$$

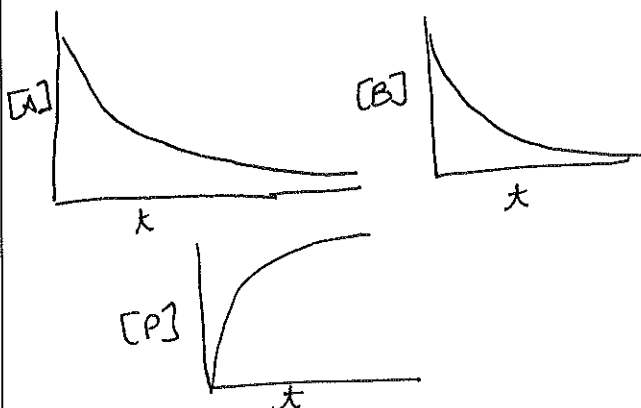


16 So, to determine whether the rxn  $A \rightarrow P$  is  $\phi$ , 1<sup>st</sup> or 2<sup>nd</sup> order in  $[A]$ , Plot all 3 possibilities & see which has best fit.

16 2<sup>nd</sup> - order Kinetics: Situation #2



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



17 If  $B_0 = A_0$ , then  $B_x = A_x$  &

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

But, we usually do not run rxns this way.

If  $B_0 \neq A_0$

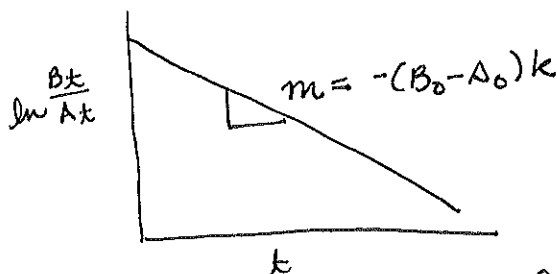
$$[B]_x = [B]_0 - ([A]_0 - [A]_x)$$

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

$$\int_0^x \frac{d[A]}{([A]([B]_0 - [A]_0) + [A]_x)} = \int_0^x -k dt$$

$$\frac{1}{(B_0 - A_0)} \ln \frac{B_x}{A_x} - \frac{1}{(B_0 - A_0)} \ln \frac{B_0}{A_0} = -kt$$

$$\begin{aligned} \Downarrow \\ kt &= \frac{1}{(B_0 - A_0)} \left( \ln \frac{B_x}{A_x} - \ln \frac{B_0}{A_0} \right) \\ \ln \frac{B_x}{A_x} &= -(B_0 - A_0)kt - \frac{1}{(B_0 - A_0)} \ln \frac{B_0}{A_0} \end{aligned}$$



In principle, just need to measure  $[A]$  &  $[B]$  at various time points.

USUALLY HARD TO DO.

19 SIMPLIFICATION: PSEUDO-FIRST-ORDER KINETICS

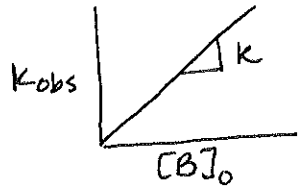
Use lots of B (≥ 10 equiv)

$$[B] \approx [B]_0$$

$$\text{rate} = \frac{d[P]}{dt} = k[A][B] \approx k[A][B]_0$$

$$\text{rate} = k_{\text{obs}}[A], \text{ where } k_{\text{obs}} = k[B]_0$$

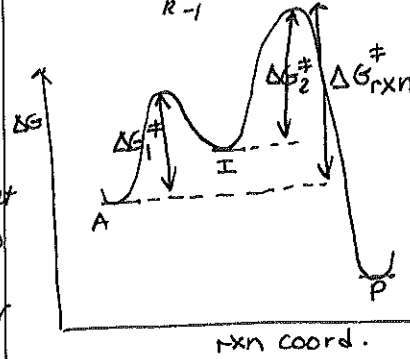
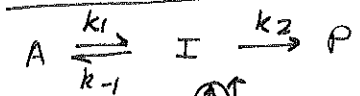
Now use 1st order treatment...



Pseudo-1st order kinetics can also be used in multistep mech's.

BUT may not represent actual rxn conditions!!

20 MULTISTEP PROCESS



Rate constants are numbered by which step they are for.  
Step 1:  $k_1$  (forward),  $k_{-1}$  (reverse)

Almost always ok to assume last step is irreversible.

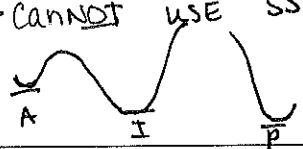
Overall rate determined by overall barrier ( $\Delta G_{\text{rxn}}^\ddagger$ )  
⇒ Combination of steps.

21 Rate of each step depends on rate constants (k's) & [SM].

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

Hard to measure I in this case.

But, [I] also won't change much (no build-up).  
WARNING: Sometime [I] will change!  
→ CANNOT USE SSA.



22 STEADY-STATE APPROXIMATION

$$\frac{d[I]}{dt} = 0 \quad (\text{NOT } [I] = 0!!!)$$

$$\frac{d[I]}{dt} = k_1[A] - k_{-1}[I] - k_2[I] = 0$$

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

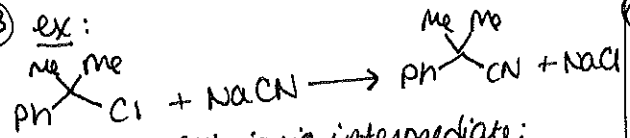
$$[I] = \frac{k_1[A]}{(k_{-1} + k_2)}$$

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

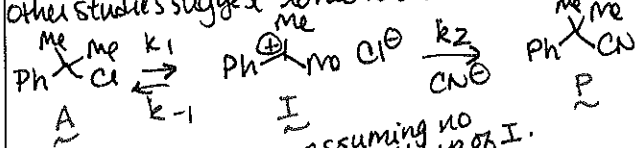
Rate in terms of A, which we can observe.

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

23 ex:



Other studies suggest ionic intermediate:



What is rds?

$$\text{Rate} = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = k_2[I][\text{CN}^-]$$

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

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

24

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

Numerator: Everything that makes prod.  
Denominator: Everything that destroys intermediates.

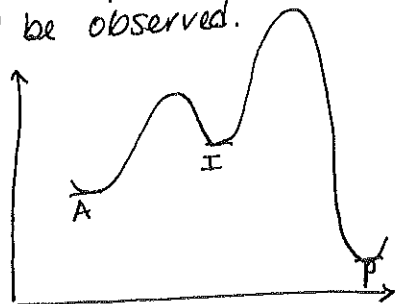
COMPLICATED!!

Rate changes as conditions change!

25) LIMITING CASES

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

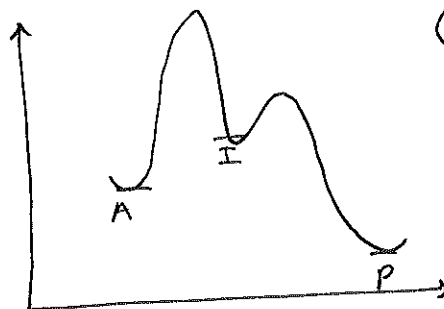
Inverse dependence on  $[Cl^-]$  will be observed.



26) If  $k_2[CN^-] \gg k_{-1}[Cl^-]$

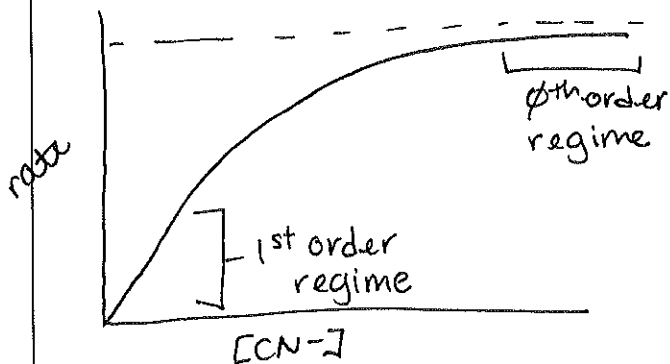
rate  $\Rightarrow \frac{k_1 k_2 [A][CN^-]}{k_2[CN^-]} \approx k_1[A]$

SN1



HEIGHTS CHANGE B/C CONCENTRATIONS, NOT K'S, CHANGE.  
 height  $\propto k_{obs}[X]$

27) Consider  $[CN^-]$  vs. rate...



Common scenario: Change in rds as rxn proceeds / based on rxn conditions.

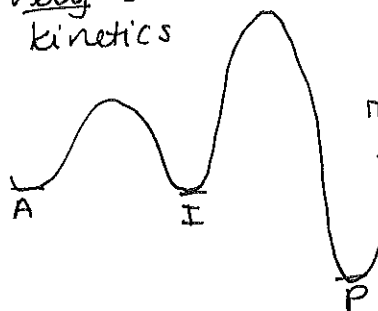
28) SATURATION KINETICS

- Seen in Asymptotic Curve.
- Adding more  $CN^-$  will not speed up rxn.
- Very common in enzyme kinetics

$$K_{eq} = \frac{[I]}{[A]}$$

$$rate = k_2 [I]$$

$$v = k_2 K_{eq} [A]$$



29) In saturation kinetics, you do have build-up of I under saturated conditions.

(Don't use SSA for saturated systems.)

If you observe saturation, you have reversible step before your rds.

30) What about non-limiting cases?

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

How do we plot data in a meaningful way?

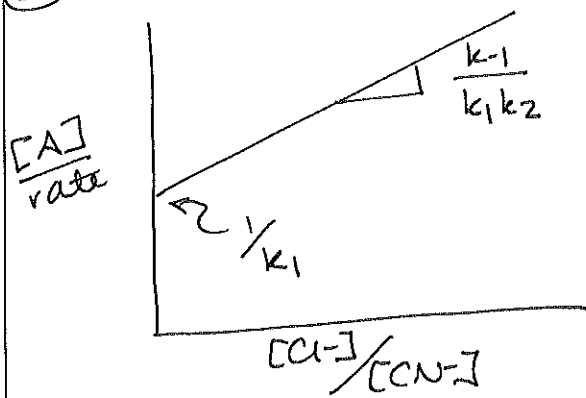
$$\frac{1}{rate} = \frac{k_{-1}[Cl^-] + k_2[CN^-]}{k_1 k_2 [A][CN^-]}$$

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

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

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

31



If you can measure concentrations,  
you can extract rate constants.

Next time: How do  
we actually measure  
concentrations & rates?