

B. Mechanism – 2009 rearrange -- Engel Ch 25.4,10,8

Series of elementary steps (uni-, bimolecular) that when combined give overall reaction and observed rate law

elementary steps have reaction order like stoichiometry

Unimolecular: $A \xrightleftharpoons[k_{-1}]{k_1} P$

1st order $-d[A]/dt = k_1[A] \rightarrow$

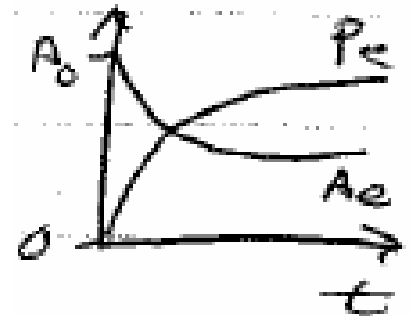
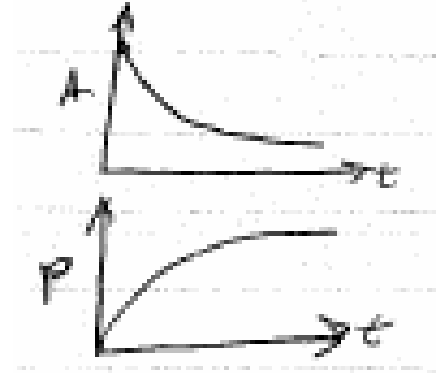
$$\ln [A]/[A_0] = -k_1 t$$

as approach equilibrium - both forward and reverse steps must be in mech.:

$$-d[A]/dt = k_1[A] - k_{-1}[P]$$

$$\text{equilibrium: } d[A]/dt = 0 = k_1[A_e] - k_{-1}[P_e]$$

$$K_{eq} = [P_e]/[A_e] = k_1/k_{-1}$$



see if product really favored: $K_{eq} \gg 1$, then $k_1 \gg k_{-1}$

\rightarrow rate law mostly like $r \sim k_1 [A]$

same *2nd order*: if elementary step $A + B \xrightleftharpoons[k_{-1}]{k_1} C + D$

$$\text{then: } r = k_1 [A] [B] - k_{-1} [C] [D]$$

$r = 0$ at equilibrium

$$K_{eq} = [C] [D] / [A] [B] = k_2/k_{-2}$$

reconsider 1st order: $r = k_1[A] - k_{-1}[P]$ $[P] = [A_0] - [A]$
 $r = k_1[A] - k_{-1}\{[A_0] - [A]\} = (k_1 + k_{-1})[A] - k_{-1}[A_0]$
 $r = (k_1 + k_{-1})\{[A] - [k_{-1}/(k_1 + k_{-1})][A_0]\}$

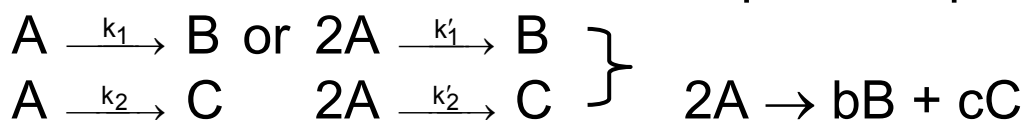
recall: $K_{eq} = [P_e]/[A_e] = (A_0 - A_e)/A_e = (A_0/A_e - 1) = k_1/k_{-1}$
 $[A_0]/[A_e] = k_1/k_{-1} + 1 = (k_1 + k_{-1})/k_{-1}$

substitution: $r = (k_1 + k_{-1})\{[A] - [A_e]\}$

let $A' = A - A_e$, then $-dA'/dt = -dA/dt = r = k'A'$

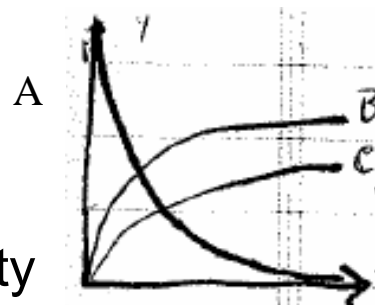
1st order → approaches an asymptote at A_{eq} - integrate
 $\ln(A - A_e)/(A_0 - A_e) = -(k_1 + k_{-1})t$

c) Alternate case – parallel reaction (2 paths for A, forms independent products)



Note: $b + c$ give ratio of product NOT stoichiometry

$$r = -1/2 d[A]/dt = k'_1[A]^2 + k'_2[A]^2 = (k'_1 + k'_2)[A]^2$$



again looks simple, could hide complexity

Chain Reaction – series of steps – find the bottleneck

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ means cannot get C without forming B

Rate Determining Steps

for chain – assume one step slowest ⇒ bottleneck



[this will be core issue for Mechanisms modeling!!]

Methods – 2009 --time dependence Engel Ch 25.11

Initial examples assume start $[R] = A_0 + B_0$ etc., $[P] = 0$

follow reaction forward → initial rate, etc. follow $[A]$

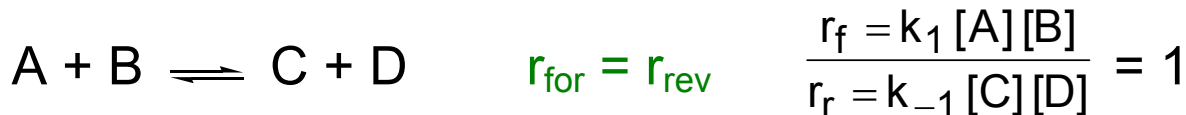
Monitor Absorbance, fluorescence, electrochemistry, ...
whatever is proportional to concentration

If reverse reaction or alternate steps important

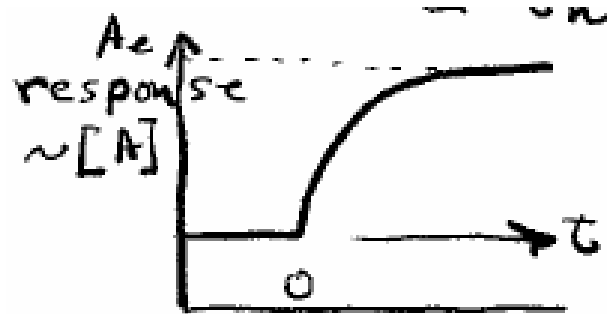
Need to monitor other species (intermediates)

At equilibrium, rates change depend on: $[R]$ & $[P]$

Equilibrium, if elementary



$$K_{\text{eq}} = k_1/k_{-1} = \frac{[C]_e [D]_e}{[A]_e [B]_e}$$

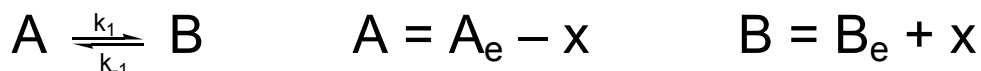


Disturb equilibrium (relaxation)

- change T, P, pH, ... **how ?** →
discharge capacitor, shock wave,
Laser flash-photolysis or T-jump

- system must relax to new equilibrium

- reaction must go forward/reverse to new state



x = departure from equilibrium at time = t , new T or P

$x = x_e e^{-t/\tau}$ relaxation time: **$1/\tau = k_1 + k_{-1}$**

$r = k_1 A - k_{-1} B = k_1(A_e - x) - k_{-1}(B_e + x) = -dA/dt =$

$dx/dt = -(k_1 + k_{-1})x + k_1 A_e - k_{-1} B_e = -(k_1 + k_{-1})x$

Note: relaxation faster if **either k_1 or k_{-1}** fast

Since $K_{\text{eq}} = k_1/k_{-1}$ get both values k_1, k_{-1} from τ & K_{eq}

Mechanism Overview: series of elementary steps (uni- or bimolecular) that combine to give observed rate law
elementary step - reaction order like stoichiometry

Sequential steps – most interesting - bottleneck

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ means need to form B to get C

Same for $A + B \rightarrow C + D$

$D + E \rightarrow E + F$, etc. D formation limit E

Characteristic induction period, how intermediate forms

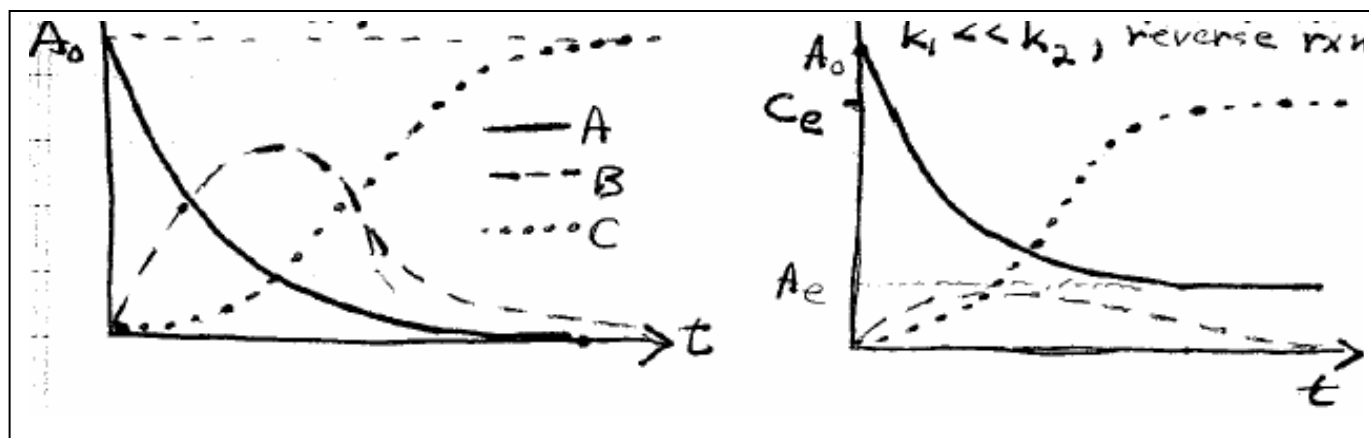
Choices (2 main models or approximations):

(a) B form fast, build up **rapid equilibrium**: $A \leftrightarrow B$

$K_{eq} = k_1/k_{-1} = [B]/[A]$ -- intermediate B balance A

(b) very little B form, immediately go off to form C

result: $d[B]/dt \sim 0$ -- **steady state** approx.



Rapid Equilibrium

Steady State

Mechanism is always a model—needs to be **tested**

-- may mean intermediate detection or sensitivity

Chain Reaction – series of steps - bottleneck

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$ means cannot get C without forming B

neglect reverse: **a)** $-d[A]/dt = k_1[A] \Rightarrow [A] = [A_0]e^{-k_1t}$

b) $d[B]/dt = k_1[A] - k_2[B] = k_1[A_0]e^{-k_1t} - k_2[B]$
integrate: $[B] = k_1[A_0]/(k_2 - k_1) [e^{-k_1t} - e^{-k_2t}]$

c) $d[C]/dt = -k_2[B]$

stoichiometry: $[C] = [A_0] - [A] - [B]$ everything from A_0
 $[C] = [A_0]\{1 - e^{-k_1t} - [k_1/(k_2 - k_1)](e^{-k_1t} - e^{-k_2t})\}$

how does this behave? $t = 0 \rightarrow B = 0, C = 0$

$t = \infty \rightarrow C_\infty = A_0$

initially, small $t \rightarrow C < B$ (early product formation slow)

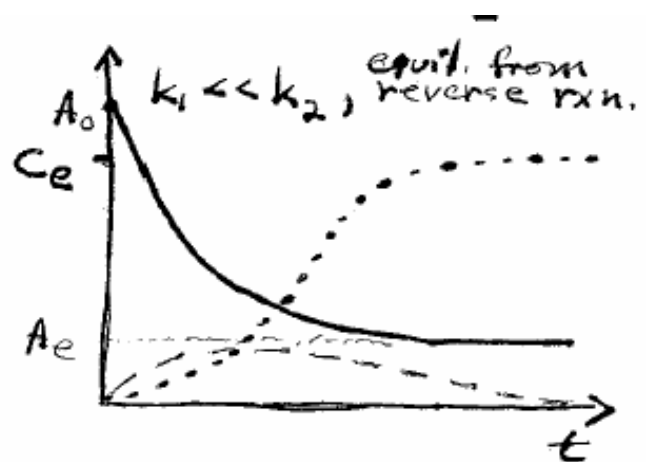
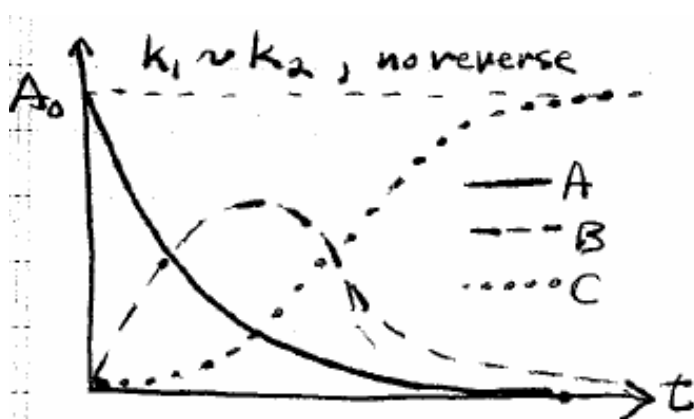
from expression for $[C]$ above – take d/dt :

$$d[C]/dt = k_1e^{-k_1t} - [k_1/(k_2 - k_1)](-k_1e^{-k_1t} + k_2e^{-k_2t})$$

induction period, $t = 0$ no product form, just intermediate

$$d[C]/dt \sim k_1 - k_1(k_2 - k_1/k_2 - k_1) \sim 0$$

$[t = \infty \quad d[C]/dt \sim 0 \quad (e^{-\infty} \rightarrow 0) \text{ -- reaction done}]$

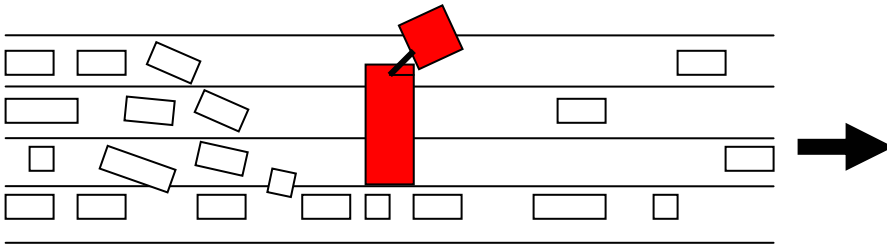


Rate Determining Steps

for chain – assume one step slowest \Rightarrow bottleneck



like expressway example: crash blocks all but 1 lane, flow of cars, $d(\text{cars})/dt$, limited by passing the truck



a) if $k_2 \gg k_1$ – as soon as B forms, it goes to C

k_1 control rate overall reaction

B concentration assume small steady value

$$d[B]/dt \sim 0 = k_1[A] - k_2[B] \quad \text{– steady state approx.}$$

$$[B] = k_1/k_2[A] \quad \text{(see graph above, right)}$$

$$d[C]/dt = k_2[B] = k_2[k_1/k_2[A]] = k_1[A] \quad \text{– looks 1}^{\text{st}} \text{ in A}$$

but should have an induction period

rearrange: $\int_0^C d[C] = \int_0^t k_1 \{ [A_0] e^{-k_1 t} \} dt$

$$[C] = [A_0] (1 - e^{-k_1 t})$$

same as before but 3rd term drops: $k_2 \gg k_1$

simpler integrated form--still has induction period

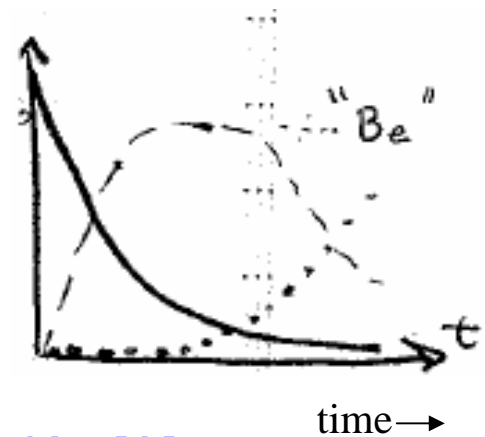
b) if $k_1 \gg k_2$ – [B] builds up and approaches equilibrium

$$d[B]/dt \approx k_1[A] = k_1[A_0]e^{-k_1 t} \quad \text{B only grows early}$$

$$[B] = [A_0] - [A] \quad \text{no decay}$$

$$d[C]/dt = k_2[B] = k_2 \{ [A_0] - [A] - [C] \}$$

early in reaction: $d[C]/dt \sim 0$
 $[C] \sim k_2 [A_0] [1/2 (e^{-k_1 t} - 1)]$



later – easier, if assume $A \xrightleftharpoons{K_e} B$
 come to rapid equilibrium

$K_e = B_e/A_e$ $d[C]/dt = k_2[B] = k_2 K_{eq} [A]$
 $\Rightarrow r = k'[A]$ again looks simple 1st order in A

both a) & b) mechanisms yield simple 1st order rate law

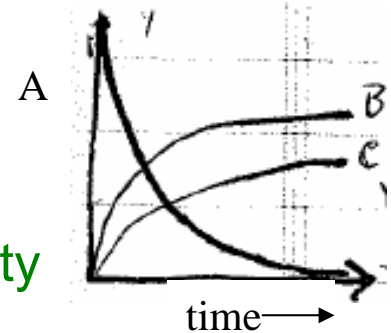
- but **complex mechanisms** behind this
- will require testing to determine complexity

c) Recall alternate – **parallel reaction** (2 paths for A,
 $A \xrightarrow{k_1} B$ or $2A \xrightarrow{k_1} B$ } independent product)
 $A \xrightarrow{k_2} C$ $2A \xrightarrow{k_2} C$ } **$2A \rightarrow bB + cC$**

Note: b & c kinetic ratio of product **NOT** stoichiometry
 second case:

$$r = -1/2 d[A]/dt = k'_1[A]^2 + k'_2[A]^2$$

$$= (k'_1 + k'_2) [A]^2$$



again looks simple, could hide complexity

How to determine complexity – for above cases:

- c) – see 2 products whose ratio is non-stoichiometric or T-dependent
- a) – see induction period in [C]
- b) – detect intermediate [B]

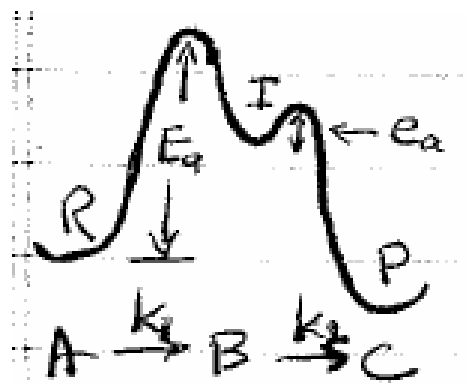
Bring ideas from **reaction coordinate / energy diagram**

1st step slow – big E_a $k_1 = A_1 e^{-E_a/RT}$

2nd step fast – small e_a $k_2 = A_2 e^{-e_a/RT}$

in this case reverse steps slow (big E_a)

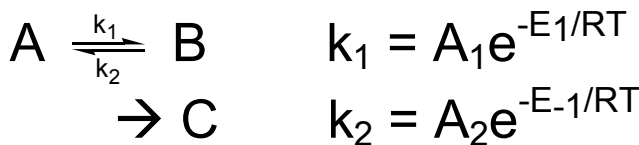
⇒ **like steady state case (a)**



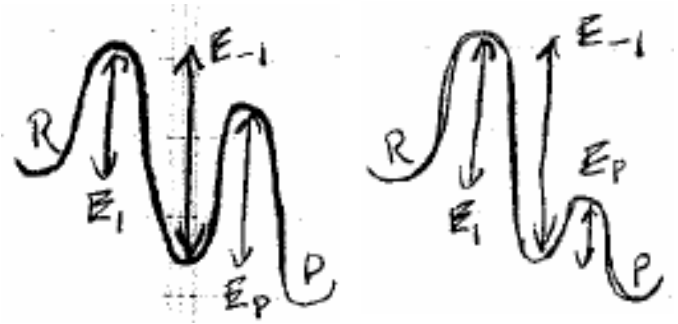
Example, Atkins & dePaula, Fig. 7.10

pre-equilibrium can have 2 types of process (A=R, P=C)

depending on **barrier from B → C** (B intermediate)



probable: $k_{-1} < k_1$ since
 $E_1 < E_{-1}$ (assume A similar)
 favors B_e: $K_e = B_e/A_e = k_1/k_{-1}$



but as increase T : k_{-1} will increase faster than k_1
 since this controls B and thus C – could slow rate

effective activation: $E_1 - E_{-1} + E_p$ **can be negative!**

Application: case study 7.1 – Protein Folding in Atkins

To study rates of helix and sheet formation, we can observe changes in IR spectra and for tertiary (fold) formation can study fluorescence after change in T