Most chemical reactions take place via a set of elementary steps, each of which involves only a few colliding partners.

$$\underbrace{H + Br_2 \longrightarrow HBr + Br}_{\text{molecularity} = 2}$$

$$\underbrace{A \longrightarrow P}_{\text{molecularity} = 1}$$

Rate laws for the elementary steps follow kinetics matching the order

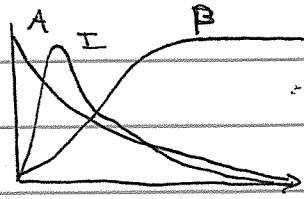
$$\frac{d[A]}{dt} = -k[A]$$

$$A + B \longrightarrow P \implies \frac{d[A]}{dt} = -k[A][B]$$

The overall reaction mechanism may have different kinetics than the elementary steps:

Consecutive reactions: $A \xrightarrow{k_a} I \xrightarrow{k_b} P$

(e.g. radioactive decay via intermediates)



$$[A](t) = [A]_0 e^{-k_a t}$$

$$[I](t) = \frac{k_a}{k_B - k_a}\left(e^{-k_a t} - e^{-k_B t}\right)[A]_0$$

$$[P](t) = \left\{1 + \frac{k_a e^{-k_B t} - k_B e^{-k_a t}}{k_b - k_a}\right\}[A]_0$$

How did we get these?

① $\frac{d[A]}{dt} = -k_A[A]$

② $\frac{d[I]}{dt} = k_A[A] - k_B[I]$ ← both elementary steps

③ $\frac{d[P]}{dt} = k_B[I]$

Solve ①, then use $\frac{dy}{dx} + y f(x) = g(x)$

(Basic Diff EQ tools: $y = e^{-\int f(x)dx}\left[\int e^{+\int f(x)dx} g(x)\,dx + c\right]$

to get ②, ③ is solved using conservation of mass.

So consecutive elementary steps (each with a simple rate law) can lead to complicated overall behavior!

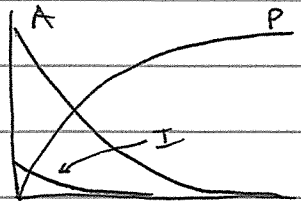
If our intermediate I is gobbled up as soon as it can be made (eg $k_B \gg k_A$) we can invoke the steady state approximation:

That is:

② $\frac{d[I]}{dt} = k_A[A] - k_B[I] \approx 0$

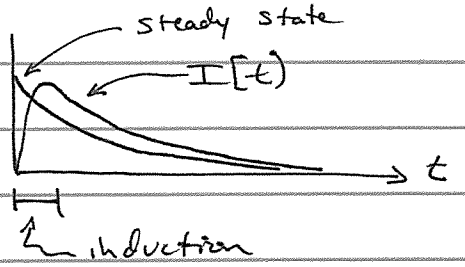
$\therefore [I](t) \approx \frac{k_A}{k_B}[A] = \frac{k_A}{k_B}[A_0]e^{-k_A t}$

③ $\frac{dP}{dt} = k_B[I] \simeq k_A e^{-k_A t}[A_0]$

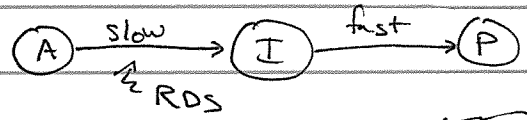


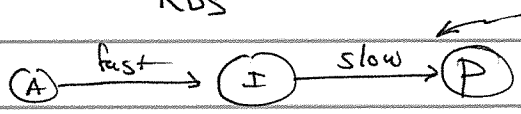
$[P](t) \approx (1 - e^{-k_A t})[A]_0$

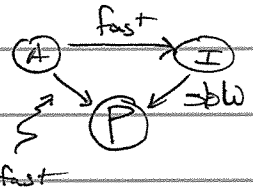
The brief window of time where steady state isn't very good is called the induction period



What the steady state approximation shows is that the overall rate usually depends most strongly on the slowest elementary or rate-determining step.







sometimes what you think is the RDS is bypassed by an alternate mechanism

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Pre-equilibrium Consider this mechanism:

$$A + B \underset{k_{a'}}{\overset{k_a}{\rightleftharpoons}} I$$

$$I \xrightarrow{k_B} P$$

If the first step comes to rapid equilibrium:

$$K_{eq} = \frac{[I]}{[A][B]} = \frac{k_a}{k_{a'}} \quad \begin{matrix} \leftarrow \text{forward} \\ \leftarrow \text{reverse} \end{matrix}$$

(only when $k_{a'} \gg k_B$) we can deduce

$$[I] \approx \frac{k_a}{k_{a'}} [A][B]$$

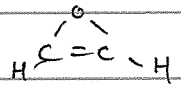
So the product rate law:

$$\frac{d[P]}{dt} = k_B[I] \approx \frac{k_a k_b}{k_a'}[A][B]$$

This approximation works at short times, but at longer times [I] keeps leaking away to form product!

Some gas phase reactions are unimolecular

$$\text{cyclo-}C_3H_6 \longrightarrow CH_3CH{=}CH_2$$

$$H_2C{=}C{=}O \longrightarrow$$ 

The Lindemann-Hinshelwood mechanism helps explain these:

(1) $A + A \xrightarrow{k_a} A^* + A$ $\qquad \frac{d[A^*]}{dt} = k_a[A]^2$

Bimolecular collision creates energetically excited A^* molecule

(2) $A + A^* \xrightarrow{k_a'} A + A$ $\qquad \frac{d[A^*]}{dt} = -k_a'[A^*][A]$

collisions can de-excite A^*

(3) $A^* \longrightarrow P$ $\qquad \frac{d[A^*]}{dt} = -k_B[A^*]$

only excited A^* can react

$$\frac{d[A^*]}{dt} = k_a[A]^2 - k_a'[A^*][A] - k_B[A^*] \approx 0$$

steady state approximation

$$[A^*] \approx \frac{k_a [A]^2}{k_B + k_a' [A]}$$

$$\frac{d[P]}{dt} = k_B [A^*] = \frac{k_a k_B [A]^2}{k_B + k_a' [A]}$$

If the rate of collisional deactivation $k_a'[A][A^*]$ is larger than the rate of decomposition $k_B[A^*]$

The Product that is formed has 1st order kinetics with $k = \frac{k_a k_B}{k_a'}$

When [A] is reduced in concentration, the kinetics turns over to 2nd order!

We determine rate laws using a few simple techniques:

a) Pseudo 1st order: Prepare samples with all reactants except 1, in great excess, so that only 1 reactant concentration at a time matters.

$v = k[A][B]$ If $[B] \approx 55\,M$ and we test

$[A] = 1M$

$[A] = 0.1M$

⋮

well figure out what the rate law in [A] must be!