11-22-99

$A + B \rightarrow C$ Stoichiometry

If actual reaction proceeds via the following mechanism

$A + A \rightarrow Q$
$Q + B \rightarrow R$
$R \rightarrow A + C$

then these are called the elementary reactions.

General "Class I" Reactions

$nA \rightarrow P$

If $v = kA^n$ then $-\frac{dA}{dt} = kA^n$

$$\int -\frac{dA}{A^n} = \int k\,dt$$

Yields:

$$\frac{1}{n-1}\left[\frac{1}{A^{n-1}} - \frac{1}{A_o^{n-1}}\right] = kt \quad (\text{for } n \neq 1)$$

As an exercise, show that:

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)\,k\,A_o^{n-1}}$$

(even OK for non-integral n)

Experiment: Determining the order of a reaction (and the rate constant)

If we look at the various equations for the different classes of reactions, we can manipulate them the way we did for Scatchard analysis.

Table 7.3 summarizes:

| | | Units of k | Linear Plot |
|---|---|---|---|
| $0^{th}$ order | $\frac{\partial C}{\partial t} = k$ | $M\,s^{-1}$ | C vs. t |
| $1^{ST}$ order | " $= kA$ | $s^{-1}$ | ln C vs. t |
| $2^{ND}$ order (I) | " $= kA^2$ | $M^{-1}\,s^{-1}$ | $1/c$ vs. t |
| $2^{ND}$ order (II) | $\frac{-dA}{dt} = kAB$ | $M^{-1}\,s^{-1}$ | $\ln C_A/C_B$ vs t |
| $n^{th}$ order ($n \neq 1$) | " $= kA^n$ | $M^{1-n}\,s^{-1}$ | $1/C^{n-1}$ vs t |

So you can try fitting/plotting your data these different ways. These look at concentration of product (or loss of reactant) vs. time. i.e. they fit the integrated rate equation.

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Alternatively (more simply) work with the direct (before integration) rate equation, but look at differential data ie. $-\frac{\partial A}{\partial t} = v$

So Plot

$v$ vs. $A$ — See directly how $v$ depends on $A$

## Method of Initial Rates – Changes in Initial Concentrations

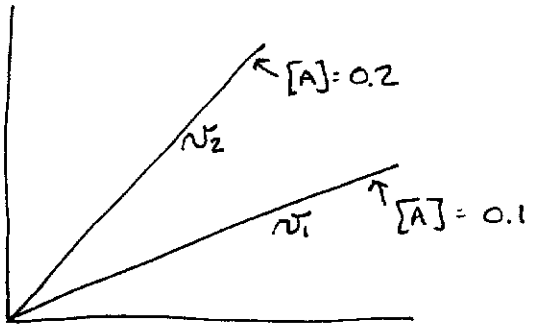
Plotting $v$ vs. A (and then B, etc) is classic!

If $v_2 = v_1$ then $\frac{v_2}{v_1} = 1 = \left(\frac{0.2}{0.1}\right)^0$

$\therefore$ $0^{th}$ order

If $v_2 = 2v_1$ then $\frac{v_2}{v_1} = 2 = \left(\frac{0.2}{0.1}\right)^1$

$\therefore$ $1^{ST}$ order




If $v_2 = 4v_1$ then $\frac{v_2}{v_1} = 4 = \left(\frac{0.2}{0.1}\right)^2$

$\therefore$ $2^{ND}$ order (class I)

It's important here to measure the (initial) rates when the concentration of the varied reagent has not decreased much (can assume that it is what you set!).

If there is more than 1 reagent, you must do this independently for each. A class II $2^{ND}$ order reaction will behave as a simpler $1^{ST}$ order reaction for each of A and B.

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Back to direct observation of C vs. t

If there is a large excess (or more) of one species, then that species effectively remains constant in concentration during time (1.00M, 0.9999M, 0.99995M, etc)

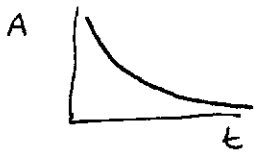
If we have $v_1 = k_1 A^a B^b C^c$

at excess C, the reaction behaves as $k_1' C^c$ ← where $k_1'$ depends on A and B

If we had $v = kAB^2C$

at excess B and C, the reaction is pseudo-first order

$v = k'A$




at excess A and C, the reaction is pseudo-2$^{ND}$ order

$v = k''B^2$


at excess A and B, .... (you fill in).

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Knowing the form of the rate law does not tell us everything about a mechanism, but it's a start.

* Knowing the rate law cannot <u>prove</u> a mechanism, but it can <u>disprove</u> some mechanisms.

↳ <u>this is a key point in kinetics</u>

We must observe <u>OCCAM'S RAZOR</u>:

"A person should not increase, beyond what is necessary, the number of entities required to explain something"

ie: choose the <u>simplest mechanism</u> which explains the data

The actual mechanism may be more complex, but one cannot propose the more complex mechanism without evidence for the more complex features.

Example: $A + B \rightarrow C$ stoichiometry

if $\frac{dC}{dt} = kA$ at excess B

and $= kB$ at excess A

then $A + B \rightarrow C$ is a good proposed mechanism

It's possible that the actual mechanism is

$$A + B \xrightarrow{\text{slow}} S \xrightarrow{\text{fast}} Q \xrightarrow{\text{fast}} Z \xrightarrow{\text{fast}} C$$

but we are not allowed to propose this without evidence for S, Q, or Z. (which would not be expected to accumulate).

THIS IS A FUNDAMENTAL PRINCIPLE of the scientific method, but is especially relevant in kinetics.

A reaction which proceeds as

$$A + B \xrightarrow[\text{react}]{\text{collide}} C$$

is bimolecular,
that is, two particles are involved in the elementary reaction.

It is therefore 2ND order overall

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However, we cannot assume that all reactions which are 2ND orders overall are bimolecular. There are other ways to observe 2ND order kinetics.

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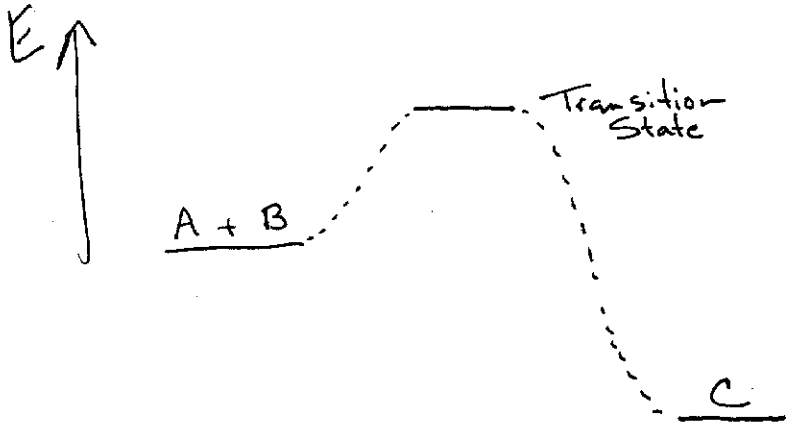
TRANSITION STATE ⇒
the state corresponding to an energy maximum on the path between two stable states



Molecularity → the number of reactant particles that come together to form the transition state in an elementary reaction.

True unimolecular reactions are unlikely — why?
Because collisional energy is required to achieve the transition state energy.

But often this collision can occur with a solvent molecule, which remains otherwise unchanged. So rate depends on temperature.

For radioactive decay, the energy comes from within (nuclear). So this is true unimolecular. (it also does not depend on temperature!)

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Termolecular (3RD order) are less likely than bimolecular, since we require 3 particles to collide simultaneously.

More common at high T and high P