

Developing Reaction Rate Models from Reaction Mechanisms

How are quantitative reaction rate models developed for complex, non-elementary reactions?

Deriving Mechanistic Rate Equation Models

1. Propose a mechanism composed of elementary reactions
Must be stoichiometrically consistent with reaction equation, i.e. must add up to rxn eqn
 2. Determine how many components/species are present in reactions
Write rate equations for each species
Then either directly solve rate equations using numerical methods or;
 3. Make assumptions regarding transition species behavior
e.g. $dx/dt = 0$, $[x]=\text{constant}$, etc.
 4. Algebraically solve for transition species concentrations and solve for measurable species rate equations
 5. Simplify/make assumptions to see if rate equations fit observed behavior
- (see examples 2.1 and 2.2 in text)

Elementary reactions

Basic assumption for elementary reactions is that the rate is proportional to the reactant concentrations, i.e.

For an elementary reaction $\nu A \rightarrow \text{products}$, the rate of reaction of A would be

$$r_A = -k C_a^{-\nu}$$

where ν is the stoichiometric coefficient and k is the reaction rate coefficient

For a reaction $-v_A A - v_B B \rightarrow \text{products}$,
the rate of reaction of A would be

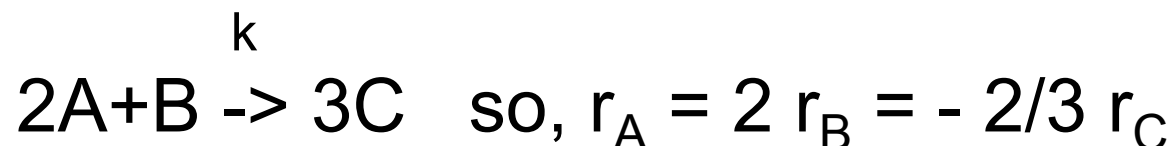
$$r_A = -k C_A^{-v_A} C_B^{-v_B}$$

Note that to maintain the stoichiometry,

$$r_B = v_B/v_A * r_A = - (v_B/v_A) k C_A^{-v_A} C_B^{-v_B}$$

i.e. if $v_A = -2$ and $v_B = -1$, then $r_A = 2 * r_B$

Irreversible elementary rxn



Assume $r_A = -2 \text{ mol/cm}_3/\text{sec}$, so

$$r_B = -1 \text{ mol/cm}_3/\text{sec} = 1/2 r_A = -1/3 r_C$$

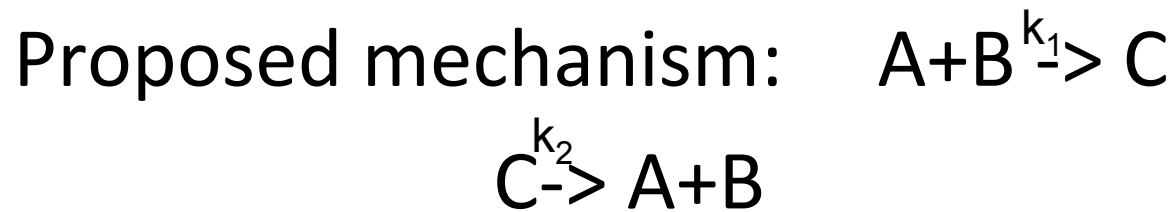
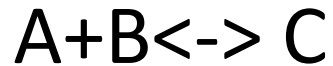
$$r_C = 3 \text{ mol/cm}_3/\text{sec} = -3/2 r_A = -3 r_B$$

The rate equations must also be consistent, so assuming $r_A = -k[A]^2[B]$, then

$$r_B = -1/2 k[A]^2[B]$$

$$r_C = 3/2 k[A]^2[B]$$

Reversible elementary rxn



Note that stoichiometry is correct

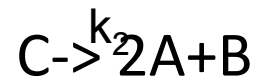
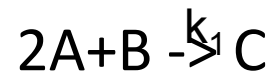
$$r_A = -k_1[A][B] + k_2[C] = r_B$$

$$r_C = k_1[A][B] - k_2[C]$$

What is the reaction rate model for this reversible elementary reaction?



First separate into 2 elementary reactions



Recognize that from overall stoichiometry, $r_A = 2 r_B = - 2r_C$

Assuming the rate eqn for component A

$$r_A = -k_1[A]^2[B] + 2 k_2 [C]$$

Rate of A being consumed rate of A being produced (why is the 2 present?)

Next, write the rate equation for B

$$r_B = - \frac{1}{2} k_1 [A]^2 [B] + k_2 [C]$$

Rate of B being consumed rate of B being produced
(why the 1/2?)

Finally, write the rate equation for C

$$r_C = + \frac{1}{2} k_1 [A]^2 [B] - k_2 [C]$$

Rate of C being consumed rate of C being produced
(why the 1/2?)

$$r_A = - k_1 [A]^2 [B] + 2 k_2 [C]$$

$$r_B = - \frac{1}{2} k_1 [A]^2 [B] + k_2 [C]$$

$$r_C = + \frac{1}{2} k_1 [A]^2 [B] - k_2 [C]$$

**Note that these rate equation satisfy the overall stoichiometry
that $r_A = 2 r_B = - 2r_C$ and that $r_B = - r_C$**

Non-elementary reaction model

The irreversible reaction



has been studied kinetically, and the rate of formation of product has been found to be well correlated by the following rate equation:

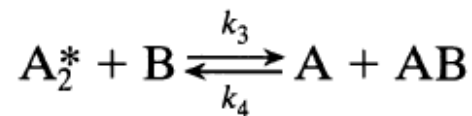
$$r_{AB} = kC_B^2 \text{ . . . independent of } C_A. \quad (11)$$

If this were an elementary reaction, the rate would be given by

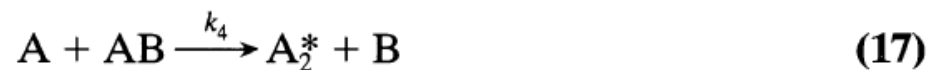
$$r_{AB} = kC_A C_B = k[A][B] \quad (12)$$

Since Eqs. 11 and 12 are not of the same type, the reaction evidently is **nonelementary**.

Model 1. Hypothesize a two-step reversible scheme involving the formation of an intermediate substance A_2^* , not actually seen and hence thought to be present only in small amounts. Thus,



which really involves four elementary reactions



$$r_{AB} = k_3[A_2^*][B] - k_4[A][AB] \quad (18)$$

$$r_{A_2^*} = \frac{1}{2} k_1[A]^2 - k_2[A_2^*] - k_3[A_2^*][B] + k_4[A][AB] \quad (19)$$

Because the concentration of A_2^* is always extremely small we may assume that its rate of change is zero or

$$\text{steady-state approximation} \quad r_{A_2^*} = 0 \quad (20)$$

$$[A_2^*] = \frac{\frac{1}{2} k_1[A]^2 + k_4[A][AB]}{k_2 + k_3[B]} \quad (21)$$

$$r_{AB} = \frac{\frac{1}{2} k_1 k_3 [A]^2 [B] - k_2 k_4 [A][AB]}{k_2 + k_3 [B]} \quad (22)$$

In searching for a model consistent with observed kinetics we may, if we wish, restrict a more general model by arbitrarily selecting the magnitude of the various rate constants. Since Eq. 22 does not match Eq. 11, let us see if any of its simplified forms will. Thus, if k_2 is very small, this expression reduces to

$$r_{AB} = \frac{1}{2} k_1 [A]^2 \quad (23)$$

If k_4 is very small, r_{AB} reduces to

$$r_{AB} = \frac{(k_1 k_3 / 2k_2) [A]^2 [B]}{1 + (k_3 / k_2) [B]} \quad (24)$$

Neither of these special forms, Eqs. 23 and 24, matches the experimentally found rate, Eq. 11. Thus, the hypothesized mechanism, Eq. 13, is incorrect, so another needs to be tried.

Model 2. First note that the stoichiometry of Eq. 10 is symmetrical in A and B, so just interchange A and B in Model 1, put $k_2 = 0$ and we will get $r_{AB} = k[B]^2$, which is what we want. So the mechanism that will match the second-order rate equation is



Enzymatic reaction rate model

A \rightarrow B mediated by enzymatic catalyst E

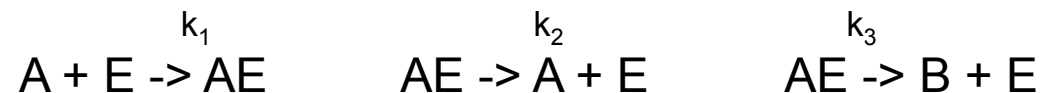
Observed hyperbolic reaction rate

$-r_A = k[A]/(k + [A])$ where k and k are rate constants

Develop a mechanistic rate model that is consistent with this observed behavior

Proposed mechanism: $A + E \rightleftharpoons AE \rightarrow B + E$

How many species are there and can you write the elementary reaction equations for this mechanism?



4 species: A, B, AE, E

Rate equations:

$$r_A = -d[A]/dt = -k_1[A][E] + k_2[AE]$$

$$r_B = d[B]/dt = k_3[AE]$$

$$r_{AE} = d[AE]/dt = k_1[A][E] - k_2[AE] - k_3[AE]$$

$$r_E = d[E]/dt = -k_1[A][E] + k_2[AE] + k_3[AE]$$

Note that AE is a transition state intermediate which is not detectable since it is very rapidly created and depleted.

Steady state assumption

Steady state assumption analysis

$$r_{AE} = k_1[A][E] - k_2[AE] - k_3[AE]$$

$$r_E = -k_1[A][E] + k_2[AE] + k_3[AE]$$

AE is a transition state intermediate which is not detectable since it is very rapidly created and depleted. Therefore, its concentration is essentially at steady state (rate of creation=rate of depletion), or $r_{AE} = d[AE]/dt = 0$.

$$r_{AE} = 0 = k_1[A][E] - k_2[AE] - k_3[AE]$$

$$[AE] = k_1[A][E]/(k_2 + k_3)$$

$$[AE] = k_1[A][E]/(k_2 + k_3)$$

$$r_B = k_3 [AE]$$

Substitute $[AE]$ into r_B equation

$$r_B = k_3 k_1[A][E]/(k_2 + k_3)$$

Assume that since all the initial enzyme, $[E]_0$, must be in either the free state, $[E]$, or bound to reactant A, $[AE]$, so by mass balance, $[E]_0 = [E] + [AE]$ so

$$[E] = [E]_0 - [AE]$$

Plugging in for $[AE]$ and solving for $[E]$ gives

$$[E] = [E]_0 (k_2 + k_3)/(k_2 + k_3 + k_1[A])$$

$$[E] = [E]_0 (k_2 + k_3)/(k_2 + k_3 + k_1[A])$$

Plugging this into the rate equation for B

$$r_B = k_3 k_1[A][E]/(k_2 + k_3) = k_3 k_1[A]([E]_0 (k_2 + k_3)/(k_2 + k_3 + k_1[A]))/(k_2 + k_3)$$

Simplifying,

$$r_B = k_3 [A][E]_0 / (k_2 + k_3 + k_1[A])$$

Gathering constant terms together,

$$r_B = k [A]/(k + [A]) = -r_A$$

Where $k = k_3[E]_0$ and $k = (k_2 + k_3)/k_1$

which is consistent with the observed hyperbolic behavior of enzymatic reactions

