

Fractional Conversion

Reaction: $aA + bB \rightarrow cC + dD$

- Conversion,
$$X_j = \frac{N_{j0} - N_j}{N_{j0}}$$

N_{j0} : initial mole of j^{th} reactant
 N_j : Final mole of j^{th} reactant

$$N_A = N_{A0}(1 - X_A)$$

$$N_B = N_{B0}(1 - X_B)$$

Representation of an Elementary Reaction

- Elementary reactions are often represented by an equation showing both the molecularity and the rate constant.



represents a bimolecular irreversible reaction with second-order rate constant k_1 , implying that the rate of reaction is

$$-r_A = r_R = k_1 C_A^2$$

- It would not be proper to write $A \xrightarrow{k_1} R$ for this would imply that the rate expression is

$$-r_A = r_R = k_1 C_A$$

- Must be careful to distinguish between the one particular equation that represents the elementary reaction and the many possible representations of the stoichiometry.

Cont..

- Writing the elementary reaction with the rate constant, may not be sufficient to avoid ambiguity. It is necessary to specify the component to which the rate constant is referred.



- If the rate is measured in terms of B, the rate equation is $-r_{\text{B}} = k_{\text{B}} C_{\text{B}} C_{\text{D}}^2$

- If it refers to D, the rate equation is $-r_{\text{D}} = k_{\text{D}} C_{\text{B}} C_{\text{D}}^2$

- Or if it refers to the product T, then $r_{\text{T}} = k_{\text{T}} C_{\text{B}} C_{\text{D}}^2$

- But from the stoichiometry $-r_{\text{B}} = -\frac{1}{2} r_{\text{D}} = \frac{1}{3} r_{\text{T}}$

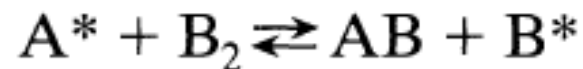
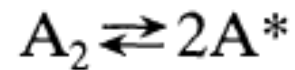
$$k_{\text{B}} = \frac{1}{2} k_{\text{D}} = \frac{1}{3} k_{\text{T}}$$

❑ Rate expression: which k? (assuming elementary reaction)

- Hence, to avoid ambiguity when the stoichiometry involves different numbers of molecules of the various components, we must specify the component being considered.

Kinetic Models for Nonelementary Reactions

- To explain the kinetics of nonelementary reactions assume that a sequence of elementary reactions is actually occurring but that we cannot measure or observe the intermediates formed because they are only present in very minute quantities.
- Observe only the initial reactants and final products, or what appears to be a single reaction.
 - If the kinetics of the reaction $A_2 + B_2 \rightarrow 2AB$ indicates that the reaction is nonelementary, we may postulate a series of elementary steps to explain the kinetics, such as



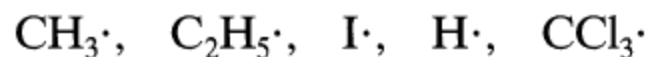
where the asterisks refer to the unobserved intermediates.

- ✓ To test our postulation scheme, we must see whether its predicted kinetic expression corresponds to experiment.

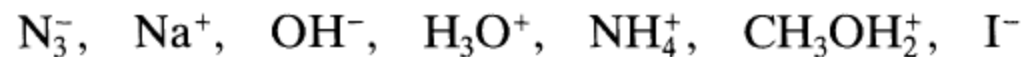
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The types of intermediates we may postulate are suggested by the chemistry of the materials. These may be grouped as follows.

Free Radicals: Free atoms or larger fragments of stable molecules that contain one or more unpaired electrons are called free radicals. Unstable and highly reactive.



Ions and Polar Substances: Electrically charged atoms, molecules, or fragments of molecules. such as



These may act as active intermediates in reactions

Cont.

Molecules. Consider the consecutive reactions $A \rightarrow R \rightarrow S$

- Ordinarily treated as multiple reactions.
- if the intermediate R is highly reactive its mean lifetime will be very small and its concentration in the reacting mixture can become too small to measure.
- In such a situation R may not be observed and can be considered to be a reactive intermediate.

Transition Complexes. The numerous collisions between reactant molecules result in a **wide distribution of energies** among the **individual molecules**.

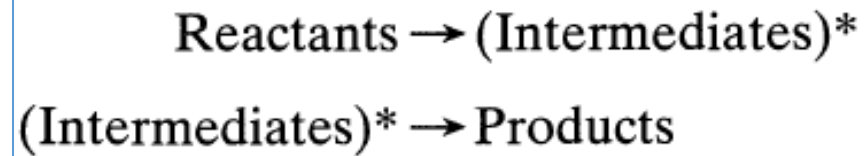
- This can result in **strained bonds, unstable forms of molecules, or unstable association of molecules** which can then **either decompose to give products, or by further collisions return to molecules in the normal state.**

Such unstable forms are called transition complexes

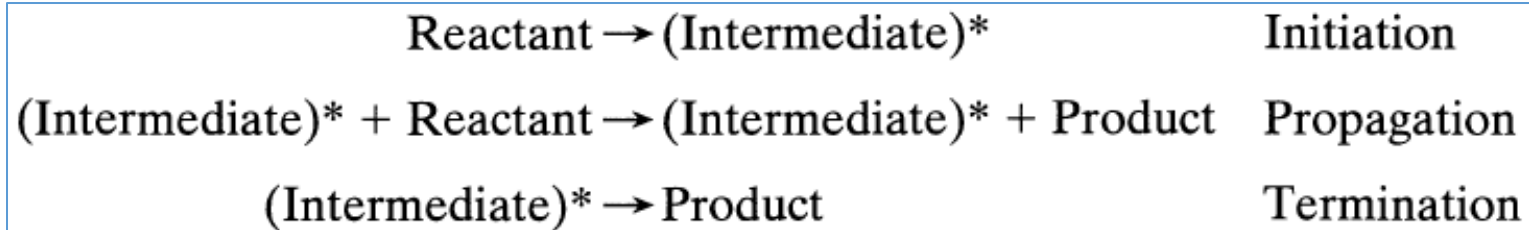
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Postulated reaction schemes involving these four kinds of intermediates can be of two types.

Nonchain Reactions: In the nonchain reaction the intermediate is formed in the first reaction and then disappears as it reacts further to give the product. Thus,



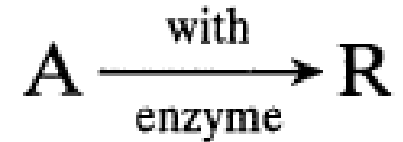
Chain Reactions: In chain reactions the intermediate is formed in a first reaction, called the *chain initiation step*. It then combines with reactant to form product and more intermediate in the *chain propagation step*. Occasionally the intermediate is destroyed in the *chain termination step*. Thus,



- The essential feature of the chain reaction is the **propagation step**. In this step the intermediate is not consumed but acts simply as a catalyst for the conversion of material. Thus, **each molecule of intermediate can catalyze a long chain of reactions, even thousands**, before being finally destroyed.

Example: Molecular intermediates, nonchain mechanism

The general class of enzyme-catalyzed fermentation reactions

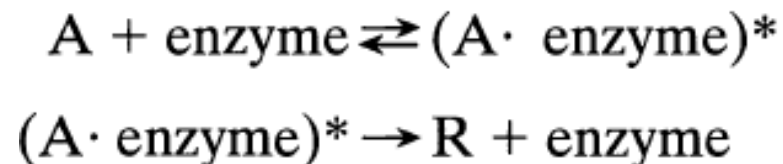


with experimental rate

$$r_R = \frac{k[A][E_0]}{[M] + [A]}$$

↖
constant

is viewed to proceed with intermediate $(A \cdot \text{enzyme})^*$ as follows:



- Proposed by Michaelis and Menten (1913)

Cont.

In these elementary reactions we hypothesize the existence of either of two types of intermediates.

Type 1. An unseen and unmeasured intermediate X usually present at such small concentration that its rate of change in the mixture can be taken to be zero. Thus, we assume

$$[X] \text{ is small and } \frac{d[X]}{dt} \cong 0$$

This is called the steady-state approximation.

Type 2. Where a homogeneous catalyst of initial concentration E_0 is present in two forms, either as free catalyst E or combined in an appreciable extent to form intermediate X, an accounting for the catalyst gives

$$[E_0] = [E] + [X]$$

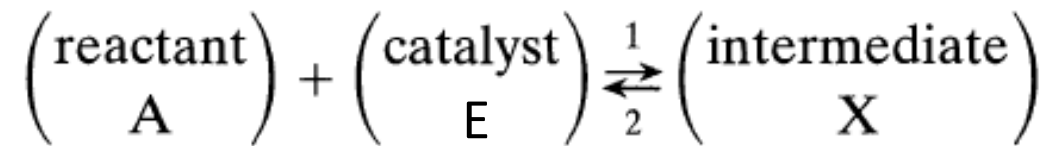
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$$[E_0]=[E]+[X]$$

We then also assume that either

$$\frac{dX}{dt} = 0$$

or that the intermediate is in equilibrium with its reactants; thus,



where

$$K = \frac{k_1}{k_2} = \frac{[X]}{[A] [E]}$$

Search for reaction mechanism

- The irreversible reaction:



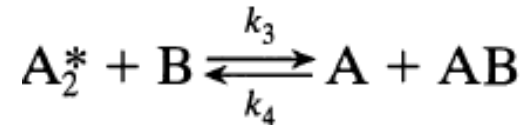
- Rate of formation of product has been found to be well correlated by the following rate equation:

$$r_{AB} = kC_B^2 \dots \text{independent of } C_A$$

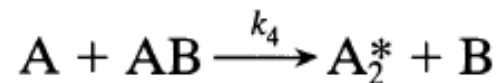
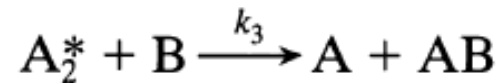
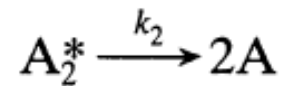
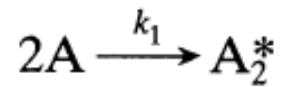
- What **reaction mechanism is suggested** by this rate expression if the chemistry of the reaction suggests that the intermediate consists of an association of reactant molecules and that a chain reaction does not occur?

Cont.

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



$$r_{AB} = k_3[A_2^*][B] - k_4[A][AB]$$

Cont.

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

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

$$r_{A_2^*} = 0$$

- This is the steady-state approximation. Combining Eqs;

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

Cont.

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

- Since predicted rate expression does not match experimental rate expression, let us see if any of its simplified forms will.

➤ Thus, if k_2 , is very small, this expression reduces to $r_{AB} = \frac{1}{2} k_1 [A]^2$

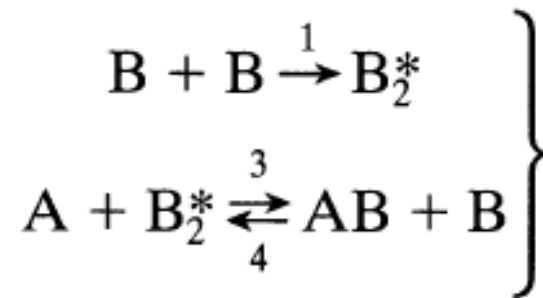
➤ If k_4 , is very small, r , reduces to $r_{AB} = \frac{(k_1 k_3 / 2 k_2) [A]^2 [B]}{1 + (k_3 / k_2) [B]}$

❑ Neither of these special forms, matches the experimentally found rate, Thus, the hypothesized mechanism, is incorrect, so another needs to be tried.

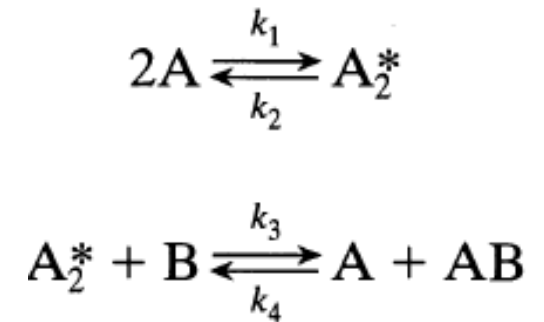
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Model 2. First note that the stoichiometry $A+B=AB$ is symmetrical in A and B, so just interchange A and B in Model 1, put $k_2 = 0$ and we will get $r_{AB}=k[B]^2$, which is what we want.

So the mechanism that will match the second order rate equation is



$$r_{AB} = (1/2) k_1 [B]^2$$



$$r_{AB} = \frac{1}{2} k_1 [A]^2$$

With $k_2 = 0$