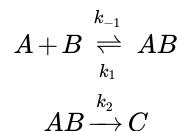


9.12: The Equilibrium Approximation

In many cases, the formation of a reactive intermediate (or even a longer lived intermediate) involves a reversible step. This is the case if the intermediate can decompose to reform reactants with a significant probability as well as moving on to form products. In many cases, this will lead to a pre-equilibrium condition in which the **equilibrium approximation** can be applied. An example of a reaction mechanism of this sort is



Given this mechanism, the application of the steady state approximation is cumbersome. However, if the initial step is assumed to achieve equilibrium, an expression can be found for $[AB]$. In order to derive this expression, one assumes that the rate of the forward reaction is equal to the rate of the reverse reaction for the initial step in the mechanism.

$$k_1[A][B] = k_{-1}[AB]$$

or

$$\frac{k_1[A][B]}{k_{-1}} = [AB]$$

This expression can be substituted into an expression for the rate of formation of the product C :

$$\frac{d[C]}{dt} = k_2[AB]$$

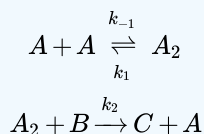
or

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}} [A][B]$$

Which predicts a reaction rate law that is first order in A , first order in B , and second order overall.

✓ Example 9.12.1:

Given the following mechanism, apply the equilibrium approximation to the first step to predict the rate law suggested by the mechanism.



Solution

If the equilibrium approximation is valid for the first step,

$$k_1[A]^2 = k_{-1}[A_2]$$

or

$$\frac{k_1[A]^2}{k_{-1}} \approx [A_2]$$

Plugging this into the rate equation for the second step

$$\frac{d[C]}{dt} = k_2[A_2][B]$$

yields

$$\frac{d[C]}{dt} = \frac{k_2 k_1}{k_{-1}} [A]^2 [B]$$

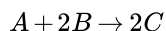
Thus, the rate law has the form

$$\text{rate} = k' [A]^2 [B]$$

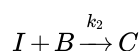
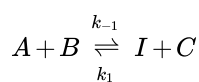
which is second order in A , first order in B and third order over all, and in which the effective rate constant (k' is

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

Sometimes, the equilibrium approximation can suggest rate laws that have negative orders with respect to certain species. For example, consider the following reaction



A proposed mechanism for which might be



in which I is an intermediate. Applying the equilibrium approximation to the first step yields

$$k_1 [A] [B] = k_{-1} [I] [C]$$

or

$$\frac{k_1 [A] [B]}{k_{-1} [C]} \approx [I]$$

Substituting this into an expression for the rate of formation of C , one sees

$$\frac{d[C]}{dt} = k_2 [I] [B]$$

or

$$\frac{d[C]}{dt} = \frac{k_1 [A] [B]}{k_{-1} [C]} [B] = \frac{k_2 k_1 [A] [B]}{k_{-1} [C]}$$

The rate law is then of the form

$$\text{rate} = k \frac{[A] [B]^2}{[C]}$$

which is first order in A , second order in B , negative one order in C , and second order overall. Also,

$$k' = \frac{k_2 k_1}{k_{-1}}.$$

In this case, the negative order in C means that a buildup of compound C will cause the reaction to slow. These sort of rate laws are not uncommon for reactions with a reversible initial step that forms some of the eventual reaction product.

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