The rate determining step is the slowest step of a chemical reaction that determines the speed (rate) at which the overall reaction proceeds. The rate determining step can be compared to the neck of a funnel. The rate at which water flows through a funnel is limited/ determined by the width of the neck of the funnel and not by the rate at which the water is poured into the funnel. Like the neck of the funnel, the slow step of a reaction determines the rate of a reaction. Not all reactions have rate determining steps and has one only if one step is significantly slower than the other steps in the reaction.

Introduction

The rate determining step is important in deriving the rate equation of a chemical reaction. For example, consider a multi-step reaction:

\[A + B \rightarrow C + D\]

Assume the elementary steps for this reaction are the following:

- Step 1: Slow \((A + A \rightarrow C + E)\) (with a rate constant, \(k_{1}\))
- Step 2: Fast \((E + B \rightarrow A + D)\) (with a rate constant, \(k_{2}\))

where E is an intermediate, the product in step 1 and a reactant in step 2 that does not show up in the overall reaction. This is because when steps 1 and 2 are added, intermediate E cancels out, along with the extra reactant A from step 1. Note that intermediate reactions do not show up in the overall reaction.

In the case of this hypothetical reaction, if step 1 is the slow step and step 2 is the fast step of the reaction, then the overall reaction rate depends on step 1; the slow step in a reaction is always the rate-limiting step, another name for the rate determining step.

Therefore the rate equation is,

\[
\text{rate} = k_{1} [A][A] = k_{1} [A]^2
\]

Example 1

Consider an example of a reaction,

\[ NO_{2 \; (g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2\; (g)}\]

which occurs in two elementary steps:

- \(NO_2 + NO_2 \rightarrow NO + NO_3 \) \text{(slow)}
- \(NO_3 + CO \rightarrow NO_2 + CO_2 \) \text{(fast)}

Because the first step is the slowest step, the overall reaction cannot be proceed any faster than the rate of the first
elementary step. The first elementary step in this example is therefore the rate-determining step. The rate equation for this reaction is equal to the rate constant of step 1 multiplied by the reactants of that first step. If the rate constant of step 1 is denoted \( k_1 \), then the rate of the first step in the reaction (and the total reaction) will be

\[
\text{rate} = k_1 [\text{NO}_2][\text{NO}_2] = k_1[\text{NO}_2]^2
\]

Example 2

A way to further understand rate-determining steps is to try to apply it to real life events. For example, consider putting together a toy that you just purchased. Let's assume that building a toy purchased from a store requires 4 steps:

1. Purchase toy parts and load into car
2. Drive toy parts to the house (or where assembly will take place)
3. Unloading toy parts from the car and take toy parts inside
4. Assemble toy.

In this example, how fast the toy is assembled will be determined by whichever of the four steps takes the longest time to complete. If there was a very long line in the toy store, then step (a) will determine the rate of assembly of the toys If the person driving the car was stuck in traffic or was driving very slowly then step (b) will determine the rate of building the toy.

Problem

A reaction between \( \text{NO} \) and \( \text{H}_2 \) occurs in the following three-step process:

\[
\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2 \; \text{(fast)}
\]

\[
\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \; \text{(slow)}
\]

\[
\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \; \text{(fast)}
\]

a. What is the rate determining step?

b. Write the balanced equation for the overall reaction.

c. Are there any intermediates? If so, state what they are.

Answer

a. The rate determining step is the second step because it's the slow step.

b. \( 2 \text{ NO} + 2 \text{ H}_2 \rightarrow \text{ N}_2 + 2 \text{ H}_2\text{O} \). This balanced reaction can be found by simply adding all 3 reactions together. In adding these reactions, the intermediates that show up on both the reactant and product side are eliminated, and the remaining species are added.

c. The intermediates in this reaction are \( \text{N}_2\text{O}_2 \) and \( \text{N}_2\text{O} \). Both of them show up on both the reactant and product side. Therefore in adding all three elementary reactions together, \( \text{N}_2\text{O}_2 \) and \( \text{N}_2\text{O} \) can be canceled out, and they will not show up in the overall reaction equation.
Sources


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