

Reaction Mechanisms

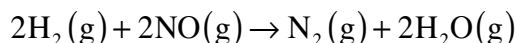
Alan D. Earhart

General Chemistry II

Goal: To learn how to evaluate a set of mechanisms to see if they fit with experimental results.

Previous Skills: A general understanding of chemical kinetics.
The ability to write a rate law from an elementary step.

For the following reaction

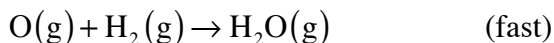
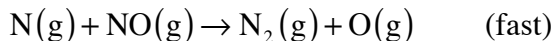
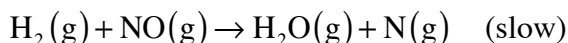


the experimentally determined rate law is

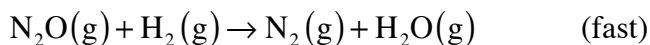
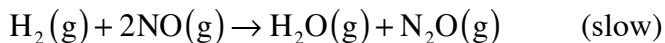
$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

For each of the following three mechanisms, state whether it is possible or not possible for it to describe the overall reaction. Show all of your work.

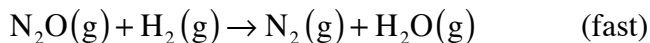
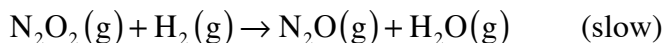
Mechanism I



Mechanism II



Mechanism III



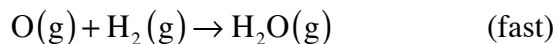
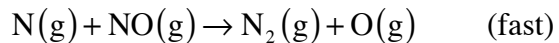
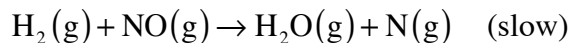
The solution is on the following pages.

Reaction Mechanisms

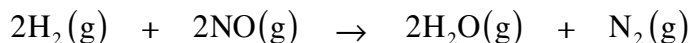
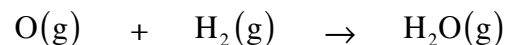
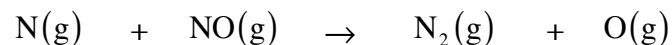
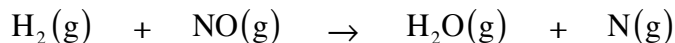
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General Chemistry II

Mechanism I



The first thing to do is verify that all the steps add up to the overall reaction (the original chemical equation).



Since the sum adds up to the original reaction, the next thing is to take the first slow step and write a rate law from it. Remember, since this is a reaction mechanism, each step is assumed to be an elementary step and the coefficients can be used to write the rate law.

Using the first step:

$$\text{rate} = k[\text{H}_2][\text{NO}]$$

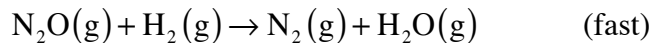
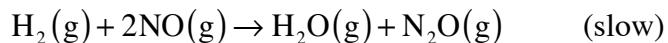
This does not match the experimentally determined rate law. Therefore, this is not a good mechanism.

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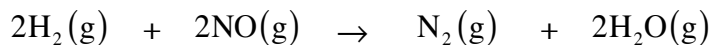
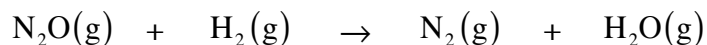
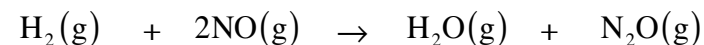
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General Chemistry II

Mechanism II



First, add the individual steps together.



This is the overall chemical equation so now the rate law needs to be verified. Working from the first slow step:

$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

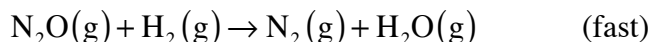
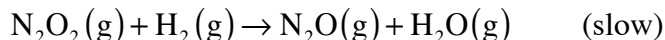
This matches the experimental rate law so this could be a good mechanism.

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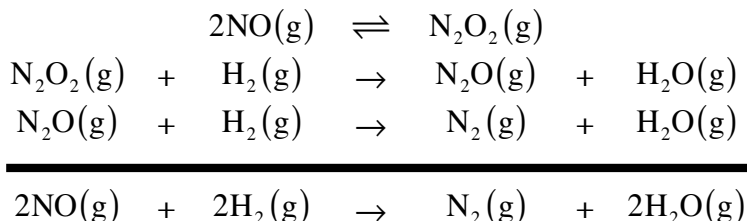
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Mechanism III



First, add the individual steps together.



These add up to the original, overall chemical equation so now we need to verify the rate law using the first slow step:

$$\text{rate} = k'[\text{N}_2\text{O}_2][\text{H}_2]$$

Although this does not match the experimentally determined rate law, we aren't finished. Recall that rate laws may not be written with reactive intermediates. N_2O_2 is a reactive intermediate (produced in one step and consumed in a later step). The first step is a fast, equilibrium step and rate laws for both the forward and reverse processes can be written:

$$\text{rate}_f = k_f[\text{NO}]^2 \quad \text{and} \quad \text{rate}_r = k_r[\text{N}_2\text{O}_2]$$

Since it is an equilibrium step, the forward rate is equal to the reverse rate:

$$k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2]$$

N_2O_2 can be solved for which yields:

$$[\text{N}_2\text{O}_2] = \frac{k_f}{k_r}[\text{NO}]^2$$

Why? Remember that the rate law from the second step contained a reactive intermediate, N_2O_2 . The preceding mathematical relationship can be used and substituted into the rate law:

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General Chemistry II

$$\text{rate} = k' \underbrace{[\text{N}_2\text{O}_2]}_{\text{intermediate}} [\text{H}_2] = k' \underbrace{\left(\frac{k_f}{k_r} \right)}_{\text{constant}} [\text{NO}]^2 [\text{H}_2]$$

This looks ugly and can be simplified. “k’”, “k_f”, and “k_r” are all constants. I can rewrite the rate law as follows:

$$\text{rate} = k [\text{NO}]^2 [\text{H}_2]$$

This does match the experimentally determined rate law and this mechanism could be a good one.