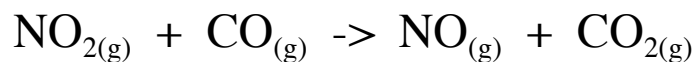


CH 222 "q&d" Guide to Reaction Mechanisms

"q&d" = "Quick 'n' Dirty"

- A **reaction mechanism** is the sequence of steps a reaction goes through at a molecular level in proceeding from reactants to products that control the speed and outcome of a reaction.
- Each step is called an **elementary step**.
- Each elementary step is called **unimolecular**, **bimolecular** or **termolecular** based upon the number of molecules colliding.
- A **reaction intermediate** is a species that is produced in one step of a reaction mechanism and completely consumed in a later step.
- The **rate law** for an elementary step does follow the balanced equation for that step.
- The slowest elementary step in a multi-step reaction mechanism is called the **rate-determining step** (RDS).
- The **sum** of the elementary steps in a multi-step reaction must give the balanced overall chemical equation.
- The mechanism must agree with the experimentally determined rate law.

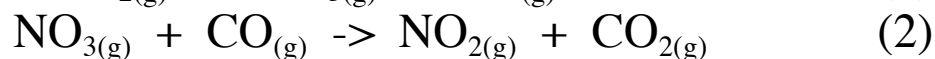
Example: The following reaction has been studied at 500 K:



An experimental rate law at 500 K has been found:

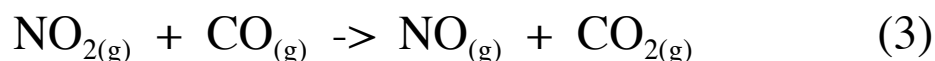
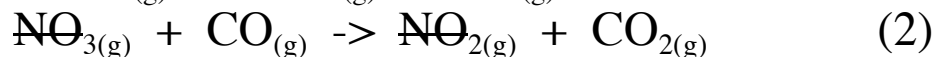
$$\text{rate} = k[\text{NO}_2]^2$$

and the following reaction mechanism proposed:



How many elementary steps are present? Is this a valid mechanism? Are there any reaction intermediates? Which step is the rate-determining step? What is the molecularity of the rate-determining step?

Solution: There are **two** elementary steps in this mechanism. To test validity, add the elementary steps together:



Reaction (3) is the same as the overall equation, so this mechanism is valid. $\text{NO}_{3(g)}$ and one molecule of $\text{NO}_{2(g)}$ are reaction intermediates. Since the rate depends on the squared concentration of $\text{NO}_{2(g)}$, elementary step (1) is the rate-determining step. The molecularity of the rate-determining step is bimolecular. The molecularity of step (2) is also bimolecular.