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:

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

An experimental rate law at 500 K has been found:

$$\text{rate} = k[NO_2]^2$$

and the following reaction mechanism proposed:

$$2\,NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)} \qquad (1)$$
$$NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)} \qquad (2)$$

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:

$$\cancel{2}\,NO_{2(g)} \rightarrow \cancel{NO}_{3(g)} + NO_{(g)} \qquad (1)$$
$$\cancel{NO}_{3(g)} + CO_{(g)} \rightarrow \cancel{NO}_{2(g)} + CO_{2(g)} \qquad (2)$$
$$\text{---------------------------------------}$$
$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)} \qquad (3)$$

Reaction (3) is the same as the overall equation, so this mechanism is valid. $NO_{3(g)}$ and one molecule of $NO_{2(g)}$ are reaction intermediates. Since the rate depends on the squared concentration of $NO_{2(g)}$, 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.