Unit 4, Lesson 06: Evaluating Reaction Mechanisms

The Rate Law for a reaction is determined **experimentally** by changing the concentration of **one reactant** at a time, while all other variables are held **constant**.

If changing the concentration of a reactant changes the reaction rate, then that reactant is involved in the **rate-determining step (RDS)**.

If changing the concentration of a reactant does not change the reaction rate, then that reactant is **not involved** in the rate-determining step (RDS).

The Rate Law for a reaction is very useful in proposing and evaluating possible reaction mechanisms.

A proposed reaction mechanism is **plausible** (possible) if:

1. the **sum** of the steps of the reaction mechanism adds up to give the overall reaction equation &
2. the **molar coefficients** of the reactants in the **RDS** agree with the **exponents** for these reactants in the Rate Law.

It is the **rate** and **molecularity** of the RDS that determines the rate and molecularity of the overall reaction.

eg. For the reaction: $2\ NO\ (g) + 2\ H_2\ (g) \rightarrow N_2\ (g) + 2\ H_2O\ (v)$

The following reaction mechanism has been proposed:

(i)	$H_{2(g)} + NO_{(g)} \rightarrow H_2O_{(g)} + N_{(g)}$	(slow)
(ii)	$N_{(g)} + NO_{(g)} \rightarrow N_{2(g)} + O_{(g)}$	(fast)
(iii)	$O_{(g)} + H_{2(g)} \rightarrow H_2O_{(g)}$	(fast)

The Rate Law for this reaction was determined experimentally to be: rate = $k\ [H_2]^1\ [NO]^1$.

Is the proposed reaction mechanism plausible?

- the rate law for the RDS (slow step) is rate = $[H_2]\ [NO]$
- the sum of the steps in the reaction mechanism adds to give the overall equation
- the molecularity of the RDS agrees with the exponents of the rate law
- therefore, the reaction mechanism is plausible for this reaction

eg. For the reaction: $N_2O_5(g) + NO\ (g) \rightarrow 3\ NO_2\ (g)$

The following reaction mechanism has been proposed:

(i)	$N_2O_5(g) \rightarrow NO_2\ (g) + NO_3\ (g)$	(fast)
(ii)	$NO(g) + NO_3\ (g) \rightarrow 2\ NO_2\ (g)$	(slow)

The Rate Law for this reaction was determined experimentally to be: rate = $k\ [N_2O_5]$.

Is the proposed reaction mechanism plausible?

- the rate law indicates that the RDS involves one molecule of N_2O_5 breaking down
- but the proposed mechanism shows the breakdown of N_2O_5 occurring quickly, so it is not the RDS
- therefore, if the rate law is correct, then the proposed mechanism is not correct (the first step must be the slow one)

Homework: Read pages 298 to 300 (begin at "Proposing and Evaluating Mechanisms).
Answer questions 17 to 20 on page 301.