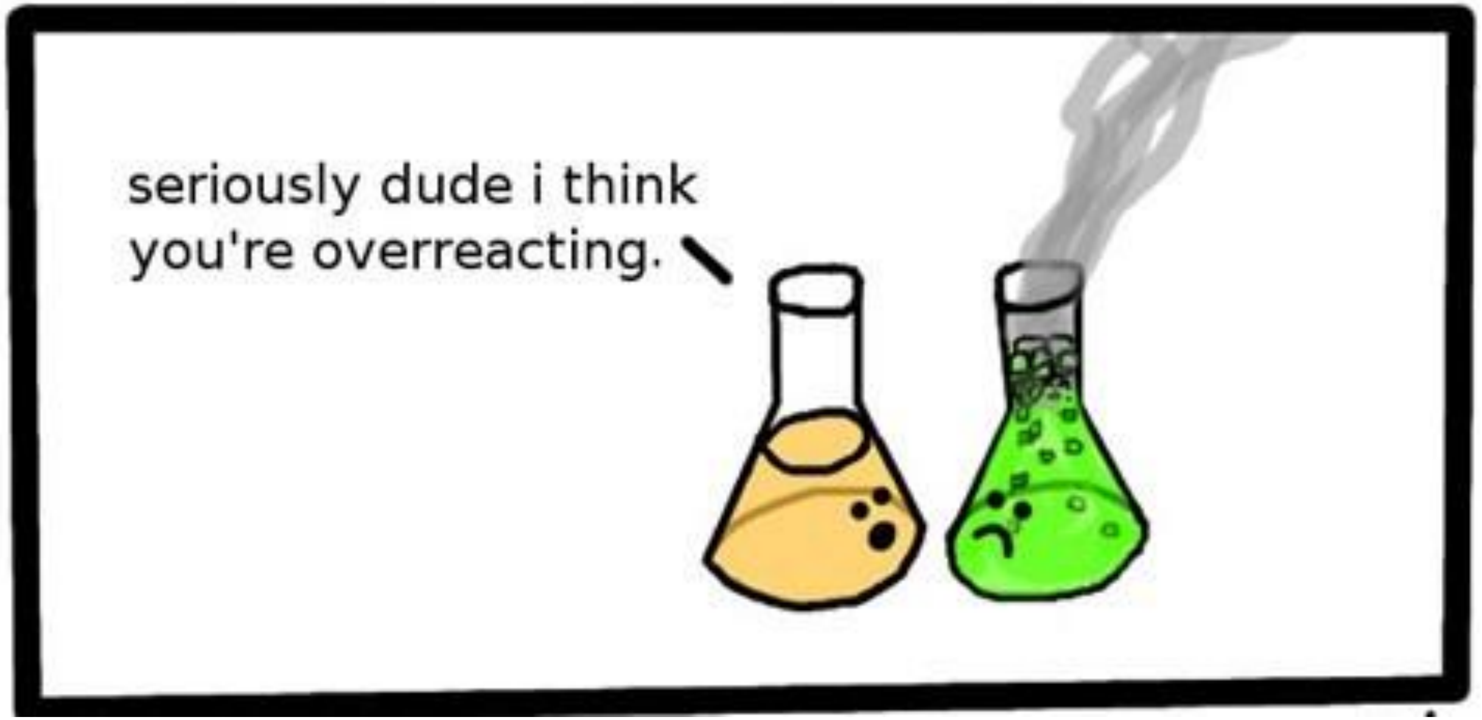
Rate Law, Stoichiometry & Mechanisms



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Outcomes:

- Determine the rate law of a chemical reaction from experimental data.

Rate Law, Stoich & Mechanisms:

Rate Law & Stoichiometry:

We have seen that for most reactions, the rate law, rate constant, and the mechanism can only be determined **EXPERIMENTALLY**.

However, for reactions that occur in a **SINGLE STEP** (**ELEMENTARY REACTIONS**), the **ORDER** of each **REACTANT** in the rate law is **EQUAL** to the **COEFFICIENT** in the **BALANCED EQUATION**.

For the ***elementary*** reaction:

$$aA + bB \rightarrow cC + dD$$

The rate law is:

$$Rate = k[A]^a[B]^b$$

Where ***a*** and ***b*** are the **MOLAR COEFFICIENTS** of the **ELEMENTARY** reaction.

Rate Law, Stoich & Mechanisms:

Example:

One reaction that results in smog occurs in an elementary single step, according to:

$$O_{3(g)} + NO_{(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

Determine the rate law.

Since the reaction occurs in one step, the coefficients are the order for each reactant, so the rate law is:

$$\textit{Rate} = k[O_3][NO]$$

Rate = k[O₃]¹[NO]¹

Rate Law, Stoich & Mechanisms:

Rate Law & Mechanism:

We have seen that rate laws for reactions that occur in **MORE** than **ONE STEP** do **NOT** correspond to the **COEFFICIENTS** of the reactants.

The rate law for these reactions corresponds to the **STOICHIOMETRY** of the **RATE DETERMINING STEP**. Reactants that are **ZERO** order, do not **APPEAR** in the **RDS**, and do not **AFFECT** the rate.

Rate Law, Stoich & Mechanisms:

Example:

The mechanism for the reaction *3M + N → P + 2Q* is:

2M → P + X	***(slow)***
X + M → Q + Y	***(moderate)***
N + Y → Q	***(fast)***

elementary rxns

a) What is the rate law?

RATE = K [M]²

b) What would be the effect of tripling [M]?

Rate ↑ 9x

Rate = K [1]² = 1K

= K [3]² = 9K

c) What would be the effect of doubling [N]?

None.

Rate Law, Stoich & Mechanisms:

Mechanisms From Rate Law:

Chemists can find a rate law experimentally, and use it to propose a mechanism for a reaction.

For the reaction,

$$2NO_{2(g)} + Cl_{2(g)} \rightarrow 2NO_2Cl_{(g)}$$

The rate law was found to be,

$$Rate = k[NO_2][Cl_2]$$

A possible mechanism would have coefficients of **1** for NO_2 and Cl_2 in the **RDS**. The **PRODUCTS** of this step would have to reflect this:

$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$$

Cl would be an **INTERMEDIATE**, and a step to follow could be:

$$NO_2 + Cl \rightarrow NO_2Cl$$

Rate Law, Stoich & Mechanisms:

To check if the mechanism is acceptable, check if the **SUM** of the steps is equal to the **NET EQUATION**:

$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$$
$$NO_2 + Cl \rightarrow NO_2Cl$$

$$2NO_{2(g)} + Cl_{2(g)} \rightarrow 2NO_2Cl_{(g)}$$

Remember, we can't find a **DEFINITE** mechanism, only a **POSSIBLE** mechanism from **EXPERIMENTAL** data.

Rate Law, Stoich & Mechanisms:

Graphical Interpretation:

Graphs of rate vs. concentration can also be used to determine reaction order: