Determining Rate Law

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6.3

Rate Laws

The rate of a reaction depends on the concentration of its reactants and/or products and/or catalysts, according to the so-called rate law for the reaction:

$$R = k\,[A]^{\alpha}[B]^{\beta}[C]^{\gamma} \ldots$$

k = rate constant
α = order with respect to A
β = order with respect to B
γ = order with respect to C
etc.

Rate Laws and Stoichiometry

- The orders that appear in the rate law for a given reaction are not determined by the stoichiometric coefficients that appear in the balanced chemical equation. They must be found from experiment.
- For example, in the reaction

  $$3H_2 + N_2 \rightarrow 2NH_3$$

  the rate is not necessarily given by the rate law

  $$R = k[H_2]^3\,[N_2]$$

Overall Reaction Order

- The overall reaction order is the sum of the orders with respect to each chemical species that appears in the rate law.
- For example, if the reaction

  $$2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$$

  has rate law $R = k\,[NO]^2\,[Br_2]$

  then the overall order is $2 + 1 = \underline{3}$

Rate Law Example

- The reaction

  $$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

  has the rate law $R = k\,[NO]^2\,[H_2]$

- Therefore the reaction is 2nd order in NO, 1st order in H_2 and 3rd order overall.

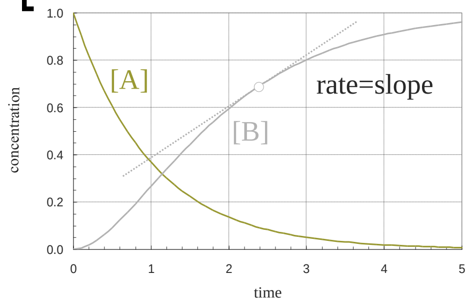
Rate Constant Units

- The units for the rate constant depend on the rate law.
- For example, if the rate law is

  $$R = k\,[NO]^2\,[Br_2]$$

  then the units are:
  - $R \sim M\ sec^{-1}$
  - $[NO] \sim [Br_2] \sim M \Rightarrow [NO]^2\,[Br_2] \sim M^3$
  - and therefore, $k \sim M^{-2}\ sec^{-1}$

Reaction Kinetics: A→B



Measured Reaction Rates

- The rate of reaction changes with time, as the concentrations of reactants and products change.
- The rate constant, but not the rate, is independent of time.
- The initial rate is the reaction rate measured before the initial concentrations have had time to change.

Determining Reaction Orders

- The rate law for a given reaction must be determined experimentally. This means determining the order with respect to each species involved.
- The two major methods are
  - Initial Rate Method
  - Integrated Rate Law Method (i.e. Calculus!!)

Initial Rate Method

Suppose the order with respect to A is α. Then $R = [A]^\alpha$. Let R_1 and R_2 be the measured rates when $[A] = [A]_1$ and $[A]_2$ respectively. Then ...

$$\frac{R_1}{R_2} = \frac{[A]_1^\alpha}{[A]_2^\alpha} = \left(\frac{[A]_1}{[A]_2}\right)^\alpha$$

$$\alpha = \ln\left(\frac{R_1}{R_2}\right) / \ln\left(\frac{[A]_1}{[A]_2}\right)$$

Initial Rate Method Example

- Suppose that doubling [A] doubles the rate.

$$\frac{R_2}{R_1} = 2 \quad = \quad \left(\frac{[A]_2}{[A]_1}\right)^\alpha = 2^\alpha \Rightarrow \alpha = 1$$

- Suppose doubling [A] quadruples the rate.

$$\frac{R_2}{R_1} = 4 \quad = \quad \left(\frac{[A]_2}{[A]_1}\right)^\alpha = 2^\alpha \Rightarrow \alpha = 2$$

Initial Rate Method Exercise

The initial rate of the reaction A + B → C was measured for several different starting concentrations as shown in the table below. Find the rate law.

Exp.	[A]	[B]	Initial Rate
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Reaction Mechanism

- The mechanism of a reaction is the sequence of individual collisions, known as elementary steps, that take the reactant molecule(s) to the product molecule(s).
- The balanced chemical equation for the reaction specifies only the reactants and products, and gives no information on the mechanism.

Rate Determining Steps

- Some reactions have a mechanism in which one of the elementary steps is much slower than the others.
- Such a slow elementary step is called the rate determining step, since it acts as the bottleneck for the overall reaction.
- The overall rate law is then simply the rate law for the rate determining step.