Rate Law

Chapter 6.5

Rate Law

- A **rate law** is the mathematical equation that allows for the calculation of reaction rate from concentration of reactants at a given temperature and pressure

Two Mathematical Expressions to Describe Reaction Rate:

$$A \longrightarrow 2B$$

1. Rate; $-\Delta[A]/\Delta t = \frac{1}{2}(+\Delta[B]/\Delta t)$
   - Determined from stoichiometry
   - Uses both reactants & products
2. Rate Law; rate $= k[A]^m$
   - Determined by experimental data- Stoichiometry of equation is irrelevant
   - Only reactants in rate law

Rate Law Equation

- The ***rate law*** expresses the relationship of the rate of a reaction to the rate constant and the **concentrations of the reactants raised to some powers.**

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

$$\text{Rate} = k\,[\text{A}]^m[\text{B}]^n$$

k is the Rate Constant

m and n are determined experimentally, and do **not** depend on stoichiometric coefficients from balanced equation

Order of Reaction

- The **order of reaction** is the exponent used to describe the relationship between the initial concentration of a particular reactant and the rate of reaction
- The reaction order tells us how quickly the rate will increase when the concentration increases

$$2A + 3B + 4C \longrightarrow \text{products}$$

$$\text{Rate} = k\,[A]^{1}[B]^{2}[C]^{0}$$

- The **total order of reaction** is the sum of the exponents in the rate law equation

Example

- The reaction

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

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

a) Determine the reaction order with respect to each of the reactants

b) Determine the overall reaction order

Order of Reaction

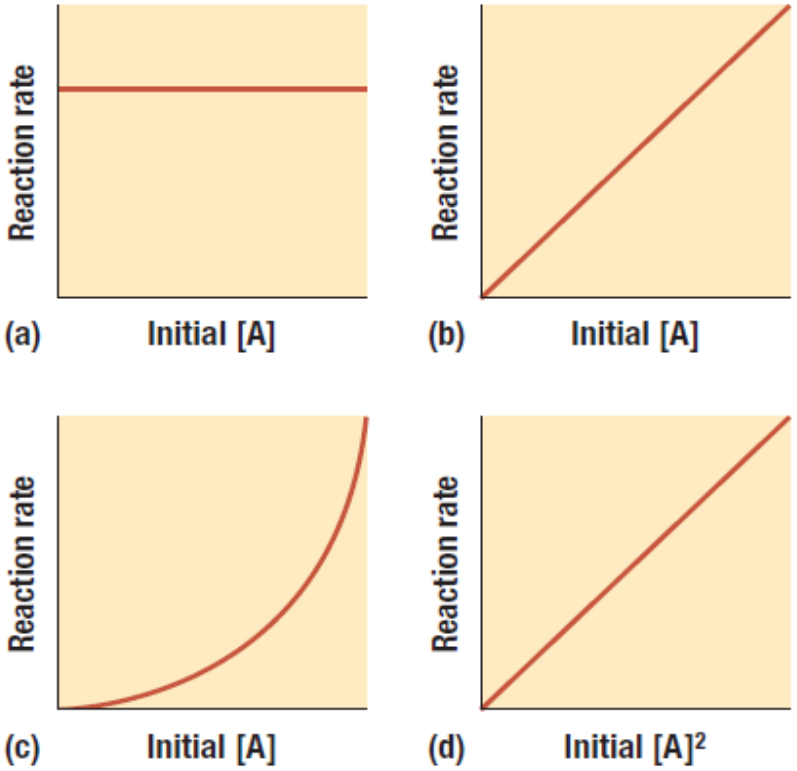

Figure 2 When a series of kinetics experiments is performed on a given system, the rates of reaction are measured for different initial concentrations of a reactant. When the evidence is graphed, you may see one or more of these results.

(a) In this plot, $r \propto [A]^0$. The reaction is zero order with respect to [A].

(b) In this plot, $r \propto [A]^1$. The reaction is first order with respect to [A].

(c) In this plot, $r \propto [A]^n$, where n is greater than 1.

(d) In this plot, $r \propto [A]^2$. The reaction is second order with respect to [A].

Determining the Exponents in a Rate Law

1. Measure the instantaneous rate of reaction before there are any significant changes in concentration of the reactants.
2. Carry out several runs using different initial concentrations, determining the initial rate resulting from each run.
3. Compare these results to observe how the initial rate depends on the initial concentrations.

Example

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

Experiment	[A] (mol/L)	[B] (mol/L)	Initial Rate (mol/L·s)
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}

Example

$$NH_4^+(aq) + NO_2^- \rightarrow N_2(g) + 2H_2O(l)$$

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.0600	0.200	32.3×10^{-7}
5	0.200	0.0202	10.8×10^{-7}
6	0.200	0.0404	21.6×10^{-7}
7	0.200	0.0606	32.4×10^{-7}
8	0.200	0.0808	43.3×10^{-7}

Find the Rate Law

HOMEWORK

Required Reading:

p. 375-382

(remember to supplement your notes!)

Questions:

p. 380 #1-5

p. 382 #1-4