Section 12.1
Chemical Reaction Rates

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Learning Objectives

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

Rates

- A **rate** is a measure of how some property varies with time.
- Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time.
- Wage is a rate that represents the amount of money earned by a person working for a given amount of time.
- The **rate of a chemical reaction** is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

We Can't See Molecules

- Because we can't count the reactants and products directly, we must measure another property that is related to the mass, mols or concentration of the these components.
  - The V, T, and P of gas from a gas evolution reaction.
  - The mass from a precipitation reaction.
  - The absorbance of a colored reactant or product.
  - Conductivity of a conductive reactant or product.
  - NMR, MS, GC-FID, HPLC, ICP-OES, etc.

Average vs. Instantaneous Rate

- You drive a car to the store ten miles away. It takes you 20 minutes to arrive there.
- Your **average rate** of speed is the distance you traveled divided by the time.

$$<v> = \frac{10 \text{ miles}}{20 \text{ minutes}} = 0.5 \ \frac{\text{mi}}{\text{min}} \quad \text{or} \quad 30 \ \frac{\text{mi}}{\text{hr}}$$

- During your trip you weren't always going 30 mph. At any given time your **instantaneous rate** of speed could have been higher or lower.

Rates of Reactions

- Reaction rates work the same way.
- The **average rate** is found by dividing the change in concentration by the time this change occurred.
- The **instantaneous rate** may be different at any given moment.
- The instantaneous rate at time zero is called the **initial rate**.
- Calculating initial and instantaneous rates properly requires calculus or sophisticated numerical methods.
  - Approximations can be made using graphical methods or by using very small time intervals.

Reaction Rate Nomenclature

- The change in species over time is the **rate expression**.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

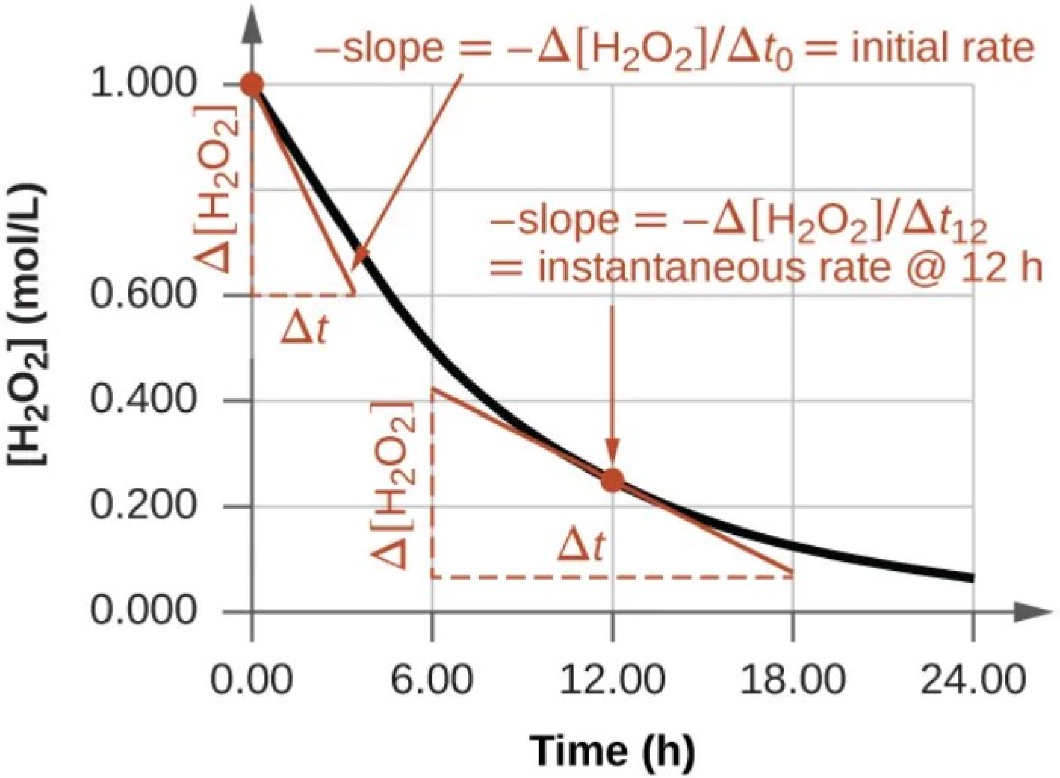
$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

Calculating Rates Numerically

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
0.00	1.000			
		−0.500	6.00	0.0833
6.00	0.500			
		−0.250	6.00	0.0417
12.00	0.250			
		−0.125	6.00	0.0208
18.00	0.125			
		−0.062	6.00	0.010
24.00	0.0625			

Graphs are your Friend

- The slope of a tangent line to a point on a time vs. concentration graph is the instantaneous rate.



Relative Rates of Reactions

- The rate of a reaction may be expressed as the change in concentration of any reactant or product.
- Rate expressions are all related simply to one another according to the reaction stoichiometry.

$$\mathrm{aA} \longrightarrow \mathrm{bB}$$

$$\mathrm{rate} = -\left(\frac{1}{\mathrm{a}}\right)\left(\frac{\Delta \mathrm{A}}{\Delta t}\right) = \left(\frac{1}{\mathrm{b}}\right)\left(\frac{\Delta \mathrm{B}}{\Delta t}\right)$$

A Practical Example

- Lets consider the example of the decomposition of ammonia.

$$2\,NH_3\ (g) \longrightarrow N_2\ (g) + 3\,H_2\ (g)$$

- The average rate of the reaction can in terms of nitrogen gas

$$\frac{\Delta \mathrm{mol}\ N_2}{\Delta t}$$

Converting Reaction Rates

- Reaction Rates can be converted using Stoichiometric Ratios.

$$\frac{\Delta \text{mol } N_2}{\Delta t} \times \frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2} = -\frac{\Delta \text{mol } NH_3}{\Delta t}$$

$$\frac{\Delta \text{mol } N_2}{\Delta t} = -\frac{1}{2}\frac{\Delta \text{mol } NH_3}{\Delta t}$$

$$\frac{\Delta \text{mol } N_2}{\Delta t} \times \frac{3 \text{ mol } H_2}{1 \text{ mol } N_2} = \frac{\Delta \text{mol } H_2}{\Delta t}$$

$$\frac{\Delta \text{mol } N_2}{\Delta t} = \frac{1}{3}\frac{\Delta \text{mol } H_2}{\Delta t}$$

Mols vs. Concentration

- We can now write the full rate equation for this reaction.

$$\text{rate} = -\frac{1}{2}\frac{\Delta \text{mol NH}_3}{\Delta t} = \frac{\Delta \text{mol N}_2}{\Delta t} = \frac{1}{3}\frac{\Delta \text{mol H}_2}{\Delta t}$$

- All of these mols occupy the same volume. Therefore we can use concentration and mols interchangeably.

$$\text{rate} = -\frac{1}{2}\frac{\Delta [\text{NH}_3]}{\Delta t} = \frac{\Delta [\text{N}_2]}{\Delta t} = \frac{1}{3}\frac{\Delta [\text{H}_2]}{\Delta t}$$

Depicting the Rates Graphically

- The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

$$\frac{2.91 \times 10^{-6}\ M/\mathrm{s}}{9.70 \times 10^{-7}\ M/\mathrm{s}} \approx 3$$