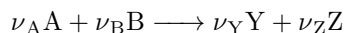


Chapter 28

Rate Laws

28.1 Definitions and Methods of Determination

- 4/8: • Consider a general chemical equation



- The extent of the reaction via the progress variable ξ is

$$n_A(t) = n_A(0) - \nu_A \xi(t) \qquad n_Y(t) = n_Y(0) + \nu_Y \xi(t)$$

- The rate of change (moles/second) is

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt} \qquad \frac{dn_Y}{dt} = \nu_Y \frac{d\xi}{dt}$$

- Deriving the rate of reaction for a gas-based chemical reaction.

- Time-dependent concentration changes

$$\frac{1}{V} \frac{dn_A}{dt} = \frac{d[A]}{dt} = -\frac{\nu_A}{V} \frac{d\xi}{dt} \qquad \frac{1}{V} \frac{dn_Y}{dt} = \frac{d[Y]}{dt} = \frac{\nu_Y}{V} \frac{d\xi}{dt}$$

- The rate (or speed) of reaction, also known as the differential rate law, is

$$v(t) = -\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_Y} \frac{d[Y]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt} = \frac{1}{V} \frac{d\xi}{dt}$$

- All terms are positive.
- Rate laws with a constant k are of the form

$$v(t) = k[A]^{m_A}[B]^{m_B}$$

- The exponents are known as **orders**.
 - The overall order reaction is $\sum m_i$.
 - The orders and overall order of the reaction depends on the fundamental reaction steps and the reaction mechanism.
- For example, for the reaction $2\text{NO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{NO}_{2(g)}$, we have

$$v(t) = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

- It follows that $v(t) = k[\text{NO}]^2[\text{O}_2]$.
- This is a rare elementary reaction that proceeds with the kinetics illustrated by the equation.
- Rate laws must be determined by experiment.
 - Multi-step reactions may have more complex rate law expressions.
 - Oftentimes, 1/2 exponents indicate more complicated mechanisms.
 - For example, even an equation as simple looking as $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ has rate law

$$v(t) = \frac{k'[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k''[\text{HBr}][\text{Br}_2]^{-1}}$$

- Determining rate laws.
 - Method of isolation.
 - Put in a large initial excess of A so that it's concentration doesn't change that much; essentially incorporates $[A]^{m_A}$ into k for determination of the order of B .
 - We can then do the same thing the other way around.
 - Method of initial rates.

- We approximate

$$v = -\frac{d[A]}{\nu_A dt} \approx -\frac{\Delta[A]}{\nu_A \Delta t} = k[A]^{m_A}[B]^{m_B}$$

- Consider two different initial values of $[B]$, which we'll call $[B_1], [B_2]$. Then

$$v_1 = -\frac{1}{\nu_A} \left(\frac{\Delta[A]}{\Delta t} \right)_1 = k[A]_0^{m_A}[B]_1^{m_B} \quad v_2 = -\frac{1}{\nu_A} \left(\frac{\Delta[A]}{\Delta t} \right)_2 = k[A]_0^{m_A}[B]_2^{m_B}$$

- Take the logarithm and solve for m_B .

$$m_B = \frac{\ln(v_1/v_2)}{\ln([B]_1/[B]_2)}$$

- Does an example problem.