Chapter 28

Rate Laws

28.1 Definitions and Methods of Determination

4/8:

- Consider a general chemical equation

$$\nu_{\mathrm{A}}\mathrm{A} + \nu_{\mathrm{B}}\mathrm{B} \longrightarrow \nu_{\mathrm{Y}}\mathrm{Y} + \nu_{\mathrm{Z}}\mathrm{Z}$$

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

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

- The rate of change (moles/second) is

$$\frac{\mathrm{d}n_A}{\mathrm{d}t} = -\nu_A\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad\qquad \frac{\mathrm{d}n_Y}{\mathrm{d}t} = \nu_Y\frac{\mathrm{d}\xi}{\mathrm{d}t}$$

- Deriving the rate of reaction for a gas-based chemical reaction.
  - Time-dependent concentration changes

$$\frac{1}{V}\frac{\mathrm{d}n_A}{\mathrm{d}t} = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -\frac{\nu_A}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t} \qquad\qquad \frac{1}{V}\frac{\mathrm{d}n_Y}{\mathrm{d}t} = \frac{\mathrm{d}[Y]}{\mathrm{d}t} = -\frac{\nu_Y}{V}\frac{\mathrm{d}\xi}{\mathrm{d}t}$$

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

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

  - 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 $2\,\mathrm{NO}_{(\mathrm{g})} + \mathrm{O}_{2(\mathrm{g})} \longrightarrow 2\,\mathrm{NO}_{2(\mathrm{g})}$, we have

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

  - It follows that $v(t) = k[\mathrm{NO}]^2[\mathrm{O_2}]$.
  - 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 $\mathrm{H_2} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{HBr}$ has rate law

$$v(t) = \frac{k'[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + k''[\mathrm{HBr}][\mathrm{Br_2}]^{-1}}$$

- 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

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

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

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

    - 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.

28.2 Integrated Rate Laws

4/11:

- First order reactions have exponential integrated rate laws.
  - Suppose $\mathrm{A} + \mathrm{B} \longrightarrow$ products.
  - Suppose the reaction is first order in A.
  - If the concentration of A is $[\mathrm{A}]_0$ at $t = 0$ and $[\mathrm{A}]$ at time t, then

$$\begin{aligned} v(t) = -\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} &= k[\mathrm{A}] \\ \int_{[\mathrm{A}]_0}^{[\mathrm{A}]} \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} &= -\int_0^t k\,\mathrm{d}t \\ \ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} &= -kt \\ [\mathrm{A}] &= [\mathrm{A}]_0 \mathrm{e}^{-kt} \end{aligned}$$

    is the integrated rate law.
  - Goes over both the concentration plot and the linear logarithmic plot.

- The half-life of a first-order reaction is independent of the initial amount of reactant.
  - The half-life is found from the point
$$[\mathrm{A}(t_{1/2})] = \frac{[\mathrm{A}(0)]}{2} = \frac{[\mathrm{A}]_0}{2}$$
  - We have
$$\ln\frac{1}{2} = -kt_{1/2}$$
$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$$
  - Notice that the above equation does not depend on [A] or [B]!
- Second order reactions have inverse concentration integrated rate laws.
  - Suppose $\mathrm{A} + \mathrm{B} \longrightarrow$ products, as before, and that the reaction is second order in A.
  - Then
$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^2$$
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} = \int_0^t k\,\mathrm{d}t$$
$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt$$
    is the integrated rate law.
- The half-life of a second-order reaction is dependent on the initial amount of reaction.
  - We have that
$$\frac{1}{[\mathrm{A}]_0/2} = \frac{1}{[\mathrm{A}]_0} + kt_{1/2}$$
$$\frac{1}{[\mathrm{A}]_0} = kt_{1/2}$$
$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0}$$
- If a reaction is n^{th}-order in a reactant for $n \geq 2$, then the integrated rate law is given by
$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^n$$
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]} -\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^n} = \int_0^t k\,\mathrm{d}t$$
$$\frac{1}{n-1}\left(\frac{1}{[\mathrm{A}]^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = kt$$
  - The associated half life is
$$\frac{1}{n-1}\left(\frac{1}{([\mathrm{A}]_0/2)^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right) = kt_{1/2}$$
$$\frac{1}{n-1}\cdot\frac{2^{n-1}-1}{[\mathrm{A}]_0^{n-1}} = kt_{1/2}$$
$$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)[\mathrm{A}]_0^{n-1}}$$

- Second order reactions that are first order in each reactant.
  - We have that

$$-\frac{\mathrm{d[A]}}{\mathrm{d}t} = -\frac{\mathrm{d[B]}}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]$$

$$kt = \frac{1}{[\mathrm{A}]_0 - [\mathrm{B}]_0} \ln \frac{[\mathrm{A}][\mathrm{B}]_0}{[\mathrm{B}][\mathrm{A}]_0}$$

  - The actual determination is more complicated (there is a textbook problem that walks us through the derivation, though).
  - When $[\mathrm{A}]_0 = [\mathrm{B}]_0$, the integrated rate law simplifies to the second-order integrated rate laws in [A] and [B].
    - In this limited case, the half-life is that of the second-order integrated rate law, too, i.e., $t_{1/2} = 1/k[\mathrm{A}]_0$.
- The reaction paths and mechanism for parallel reactions.
  - Suppose A can become both B and C with respective rate constants k_B and k_C.
  - Then

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_B[\mathrm{A}] - k_C[\mathrm{A}] = -(k_B + k_C)[\mathrm{A}] \qquad \frac{\mathrm{d[B]}}{\mathrm{d}t} = k_B[\mathrm{A}] \qquad \frac{\mathrm{d[C]}}{\mathrm{d}t} = k_C[\mathrm{A}]$$

  - The integrated rate laws here are

$$[\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-(k_B+k_C)t} \quad [\mathrm{B}] = \frac{k_B}{k_B + k_C}[\mathrm{A}]_0 \left(1 - \mathrm{e}^{-(k_B+k_C)t}\right) \quad [\mathrm{C}] = \frac{k_C}{k_B + k_C}[\mathrm{A}]_0 \left(1 - \mathrm{e}^{-(k_B+k_C)t}\right)$$

  - The ratio of product concentrations is

$$\frac{[\mathrm{B}]}{[\mathrm{C}]} = \frac{k_B}{k_C}$$

  - The yield Φ_i is the probability that a given product i will be formed from the decay of the reactant

$$\Phi_i = \frac{k_i}{\sum_n k_n} \qquad \sum_i \Phi_i = 1$$

- Example: If we have parallel reactions satisfying $k_B = 2k_C$, then

$$\Phi_C = \frac{k_C}{k_B + k_C} = \frac{k_C}{2k_C + k_C} = \frac{1}{3}$$