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

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

28.3 Office Hours (Tian)

- Why does the reduced mass work in the collision frequency derivation?
  - We need to start with a simpler case, or the problem will be really hard; thus, we begin by assuming that the particles all are static.
  - We use the reduced mass to consider the relative speed u_r of the particles with respect to the moving particle as our reference frame. So all the others are the relative speeds to our particle. But this necessitates using the relative mass of the particles to our particle (which is the reduced mass).

28.4 Reversible Reactions

4/13:

- Let

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B}$$

be a reversible reaction, where k_1 is the rate constant for the forward reaction and k_{-1} is the rate constant for the reverse reaction.

  - In this case, we have an equilibrium constant expression

$$K_c = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}}$$

  - Additionally, the kinetic conditions for equilibrium are

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = 0$$

  - If the reaction is first order in both [A] and [B], then

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}]$$

  - If $[\mathrm{A}] = [\mathrm{A}]_0$ at $t = 0$, then $[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}]$ and

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = (k_1 + k_{-1})[\mathrm{A}] - k_{-1}[\mathrm{A}]_0$$

    - Note that $[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}]$ iff there is no initial concentration of B, the initial equation was balanced (i.e., each unit of A forms one unit of B), and there is not another component C into which A decomposes.

  - Integrating yields

$$[\mathrm{A}] = ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}})\mathrm{e}^{-(k_1+k_{-1})t} + [\mathrm{A}]_{\mathrm{eq}}$$

    - Note that this equation reduces to the irreversible first order equation as $k_{-1} \to 0$ and hence $[\mathrm{A}]_{\mathrm{eq}} \to 0$ as well.
    - Similarly, if only the reverse reaction takes place (and we have no initial concentration of B), then $[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}}$ and the above equation reduces to exactly that statement, as desired.

  - Since

$$\ln([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) = \ln([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}) - (k_1 + k_{-1})t$$

    we have a straight line that allows us to determine the sum $k_1 + k_{-1}$. However, we cannot determine each term individually from the above.

  - One way that we can is by noting that at equilibrium, $\mathrm{d}[\mathrm{A}]/\mathrm{d}t = 0$, so the differential rate law reduces to

$$k_1[\mathrm{A}]_{\mathrm{eq}} = k_{-1}[\mathrm{B}]_{\mathrm{eq}}$$

  - Another way we can resolve each term individually is by noting that

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_c$$

- **Stopped flow method**: Fast mixing of reactants.
  - The limit is about 1 microsecond time resolution (mixing rate).
  - Lots of issues?
- **Pump-probe method**: An optical/IR method that ranges from femtoseconds to nanoseconds.

– Nobel Prize (1999) to Zewail "for his studies of the transition states of chemical reactions using femtosecond spectroscopy."

- **Perturbation-Relaxation method**: You perturb a thermodynamic variable (e.g., T, P, pH, etc.) and then follow the kinetics of relaxation of the system to equilibrium.

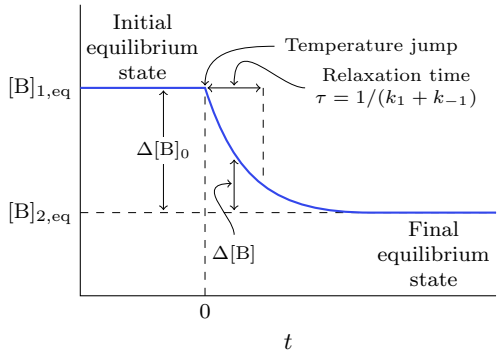

Figure 28.1: Relaxation methods to determine rate constants.

– Nobel Prize (1967) to Porter, Norrish, and Eigen "for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy."

– Example: Consider water autoionization. Here, we'd perturb pH and T.

– Our initial point is the first equilibrium condition; out final point is the second equilibrium condition (i.e., that with the perturbed variables).

– We should have

$$[\mathrm{A}] = [\mathrm{A}]_{2,\mathrm{eq}} + \Delta[\mathrm{A}] \qquad\qquad [\mathrm{B}] = [\mathrm{B}]_{2,\mathrm{eq}} + \Delta[\mathrm{B}]$$

so that

$$\frac{\mathrm{d}\Delta[\mathrm{B}]}{\mathrm{d}t} = k_1[\mathrm{A}]_{2,\mathrm{eq}} + k_1\Delta[\mathrm{A}] - k_{-1}[\mathrm{B}]_{2,\mathrm{eq}} - k_{-1}\Delta[\mathrm{B}]$$

– The sum of the concentrations is constant, so $\Delta([\mathrm{A}] + [\mathrm{B}]) = \Delta[\mathrm{A}] + \Delta[\mathrm{B}] = 0$.

– Additionally, detailed balance is satisfied.

$$k_1[\mathrm{A}]_{2,\mathrm{eq}} = k_{-1}[\mathrm{B}]_{2,\mathrm{eq}}$$

– As a result,

$$\frac{\mathrm{d}\Delta[\mathrm{B}]}{\mathrm{d}t} = -(k_1 + k_{-1})\Delta[\mathrm{B}]$$

– Integrating yields

$$\Delta[\mathrm{B}]_0 = [\mathrm{B}]_{1,\mathrm{eq}} - [\mathrm{B}]_{2,\mathrm{eq}} = \Delta[\mathrm{B}]_0 \mathrm{e}^{-t/\tau}$$

where τ is the **relaxation time**.

– It follows that

$$\Delta[\mathrm{B}] = \Delta[\mathrm{B}]_0 \mathrm{e}^{-(k_1+k_{-1})t}$$

– Some textbooks use different notation; we should know this, too.

  ■ They denote by ξ or ξ_0 the difference between [A] (the initial equilibrium's concentration) and $[\mathrm{A}]_{eq}$ (the final equilibrium's concentration).

  ■ They also use k_A, k_B for the initial equilibrium $\mathrm{A} \underset{k_B}{\overset{k_A}{\rightleftharpoons}} \mathrm{B}$ and k_A^+, k_B^+ for the final equilibrium $\mathrm{A} \underset{k_B^+}{\overset{k_A^+}{\rightleftharpoons}} \mathrm{B}$.

- **Relaxation time**: The following quantity. *Denoted by* $\boldsymbol{\tau}$. *Given by*

$$\tau = \frac{1}{k_1 + k_{-1}}$$

- We'll start with water dissociation next lecture.