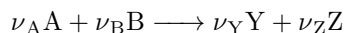


Chapter 28

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.

28.2 Integrated Rate Laws

4/11:

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

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

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

$$[A(t_{1/2})] = \frac{[A(0)]}{2} = \frac{[A]_0}{2}$$

- 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 $A + B \longrightarrow$ products, as before, and that the reaction is second order in A.
 - Then

$$-\frac{d[A]}{dt} = k[A]^2$$

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]^2} = \int_0^t k \, dt$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

is the integrated rate law.

- The half-life of a second-order reaction is dependent on the initial amount of reaction.
 - We have that

$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

- If a reaction is n^{th} -order in a reactant for $n \geq 2$, then the integrated rate law is given by

$$-\frac{d[A]}{dt} = k[A]^n$$

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]^n} = \int_0^t k \, dt$$

$$\frac{1}{n-1} \left(\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = kt$$

- The associated half life is

$$\frac{1}{n-1} \left(\frac{1}{([A]_0/2)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = kt_{1/2}$$

$$\frac{1}{n-1} \cdot \frac{2^{n-1} - 1}{[A]_0^{n-1}} = kt_{1/2}$$

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$$

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

- We have that

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

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

- The actual determination is more complicated (there is a textbook problem that walks us through the derivation, though).

- When $[A]_0 = [B]_0$, 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., $t_{1/2} = 1/k[A]_0$.

- 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

$$\frac{d[A]}{dt} = -k_B[A] - k_C[A] = -(k_B + k_C)[A] \quad \frac{d[B]}{dt} = k_B[A] \quad \frac{d[C]}{dt} = k_C[A]$$

- The integrated rate laws here are

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

- The ratio of product concentrations is

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

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

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

- 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)

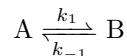
- Why does the reduced mass work in the collision frequency derivation?

- 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



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

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

- Additionally, the kinetic conditions for equilibrium are

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

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

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

- If $[A] = [A]_0$ at $t = 0$, then $[B] = [A]_0 - [A]$ and

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

- Note that $[B] = [A]_0 - [A]$ 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

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

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

- Since

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

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, $d[A]/dt = 0$, so the differential rate law reduces to

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

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

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

- **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.

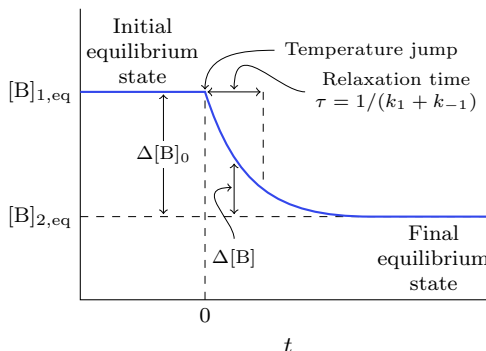


Figure 28.1: Relaxation methods to determine rate constants.

- 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; our final point is the second equilibrium condition (i.e., that with the perturbed variables).
- We should have

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

so that

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

- The sum of the concentrations is constant, so $\Delta([A] + [B]) = \Delta[A] + \Delta[B] = 0$.
- Additionally, detailed balance is satisfied.

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

- As a result,

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

- Integrating yields

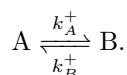
$$\Delta[B]_0 = [B]_{1,eq} - [B]_{2,eq} = \Delta[B]_0 e^{-t/\tau}$$

where τ is the **relaxation time**.

- It follows that

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

- 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 $[A]_{eq}$ (the final equilibrium’s concentration).
 - They also use k_A, k_B for the initial equilibrium $A \xrightleftharpoons[k_B]{k_A} B$ and k_A^+, k_B^+ for the final equilibrium



- **Relaxation time:** The following quantity. Denoted by τ . Given by

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

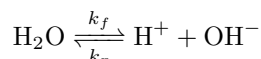
- We'll start with water dissociation next lecture.

28.5 Water Dissociation, Temperature Dependence, and TST

4/15:

- **T-jump:** A temperature perturbation.
- Relaxation methods and water dissociation.

- Consider the equilibrium



- The differential rate laws are

$$\frac{d[\text{H}_2\text{O}]}{dt} = -k_f[\text{H}_2\text{O}] + k_r[\text{H}^+][\text{OH}^-] \quad \frac{d[\text{H}^+]}{dt} = k_f[\text{H}_2\text{O}] - k_r[\text{H}^+][\text{OH}^-]$$

- After the T-jump, the system relaxes to a new equilibrium

$$K_c = \frac{k_f^+}{k_r^+} = \frac{[\text{H}^+]_{eq}[\text{OH}^-]_{eq}}{[\text{H}_2\text{O}]_{eq}}$$

- It follows that

$$\begin{aligned} \frac{d\xi}{dt} &= -k_f^+[\text{H}_2\text{O}] + k_r^+[\text{H}^+][\text{OH}^-] \\ &= -k_f^+\xi - k_r^+\xi([\text{H}^+]_{eq} + [\text{OH}^-]_{eq}) + O(\xi^2) \end{aligned}$$

- Note that we get from the first line to the second by substituting $[\text{H}^+] = [\text{H}^+]_{eq} - \xi$ and $[\text{OH}^-] = [\text{OH}^-]_{eq} - \xi$ and expanding.

- The associated relaxation time is

$$\frac{1}{\tau} = k_f^+ + k_r^+([\text{H}^+]_{eq} + [\text{OH}^-]_{eq})$$

- Note that this implies that this relaxation time can be measured experimentally.

- Rates of reaction depend on temperature.
- The empirical temperature dependence of the rate constant k is given by

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

- If the activation energy is independent of temperature, then

$$\begin{aligned} \ln k &= \ln A - \frac{E_a}{RT} \\ k &= Ae^{-E_a/RT} \end{aligned}$$

i.e., we get the Arrhenius equation.

- If we obtain two rate constants at two temperatures, we can get

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Note that plots of k vs. $1/T$ can be nonlinear if the prefactor or “encounter frequency” is temperature-dependent, i.e., if we have

$$k = aT^m e^{-E'/RT}$$

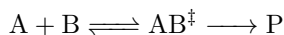
where a , E' , and m are temperature-independent constants.

- Using Transition State Theory (TST) to estimate rate constants.

- Let the following be a chemical reaction and its rate law.



- Suppose that the reaction proceeds by way of a special intermediate species, the activated complex.



- We know that

$$K_c^\ddagger = \frac{[AB^\ddagger]/c^\circ}{[A]/c^\circ[B]/c^\circ} = \frac{[AB^\ddagger]c^\circ}{[A][B]}$$

where c° is the standard-state concentration.

- Write the equilibrium constant expression in terms of the partition functions q_A , q_B , and q^\ddagger for A, B, and AB^\ddagger .

$$K_c^\ddagger = \frac{(q^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

- If ν_c is the frequency of crossing the barrier top, then

$$\frac{d[P]}{dt} = k[A][B] = \nu_c[AB^\ddagger] = \nu_c \frac{[A][B]K_c^\ddagger}{c^\circ}$$

- Thus, we can relate

$$k = \frac{\nu_c K_c^\circ}{c^\circ}$$

- 2 hour midterm at the end of this month (April) taken at home.

28.6 Office Hours (Tian)

- Stopped flow method?

- Two syringes have substances that get mixed and then become a homogeneous mixture where they start to do all of the interesting chemistry. Before the substances enter the chamber, though, they pass by a detector that monitors the concentration of the initial species. Concentration is measured after good mixing.
- It is called *stopped* flow because we want to fix the initial concentration of A and B. Inject them, let them mix, stop the flow, measure the concentration, and then let the chemistry proceed.
- Only used if mixing is much faster than reaction.
- This is the experimental set-up for the method of initial rates or the method of exhaustion.
- Caveats/issues: Approximating Δt as dt .

- TST diagram lines?

- The quantized states lines refer to the energy levels of the reactants and products summarized by the partition function.

- The reactants reach the activated complex just at some higher quantized energy state!
- Physical interpretation of τ beyond the time it takes the initial reactants to reach $1/e$ of their initial concentration.
 - You wanna see how fast the transition/relaxation would be, and τ is just a measure of how fast the transition goes.
 - Also relates to k_1 and k_{-1} .
 - Think in terms of adaptability (biological systems). Relation to how fast you can adapt to things like new temperature changes. We want to adapt to environmental changes as fast as possible.
 - A measure of adaptability, response time, and smart materials that labs are developing to respond to changes very quickly. Also instrumentation response time (which you want to be very fast).
 - Sometimes, you don't want to adapt to changes too quickly (such as cold-blooded animals).
- Importance of Chapter 24 (or 26, depending on edition)?
 - Good to know general stuff/big picture ideas as a prerequisite.
 - Don't worry about specific things tho.
- Pump-probe method?
 - No further discussion of it in this chapter; Tian might talk about it more in later chapters, tho.
 - Mostly for intra-molecular reactions, like accessing excited states and seeing how they decay.
 - Optical pumping (from IChem I, PSet 8) is one way to do a pump-probe experiment.
- Parallel reactions?
 - Behave much the same kinetically as others; only difference is there is a yield.

28.7 TST and Overview of Mechanisms

4/18:

- More TST theory.
 - We can intuitively rationalize concentration as q/V by thinking of the partition function in some way giving some information about the number of particles. When we divide this by V , we thus get *some* information about concentration.
 - δ is the finite window in which the activated complex is loosely defined to exist.
 - ν_c is the frequency of crossing the δ region in the energy diagram.
 - We substitute $[AB^\ddagger] = [A][B]K_c^\ddagger/c^\circ$ from the equilibrium constant expression.
 - The translational partition function plays a role. Note that m^\ddagger is the mass of the activated complex.

$$q_{\text{trans}} = \frac{\sqrt{2\pi m^\ddagger k_B T}}{h} \delta$$

- Dimensional analysis (as an analysis of units to help appreciate the term): $k_B T$ is energy ($E \propto mv^2/2$) and m^\ddagger is mass, so their product is momentum squared ($p^2 \propto mv^2$).
- Thus, the top of the expression gives momentum, and h/δ also gives momentum.
- Remember that the momentum is rather like that of the particle in a box.
- We have that

$$q^\ddagger = q_{\text{trans}}^\ddagger \cdot q_{\text{rot}}^\ddagger$$

where q^\ddagger is the partition function for the whole species, which we can split.

- This permits

$$K_c^\ddagger = \frac{(q^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)} \\ = \frac{\sqrt{2\pi m^\ddagger k_B T}}{h} \delta \frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

and the following

$$k = \nu_c \frac{\sqrt{2\pi m^\ddagger k_B T}}{hc^\circ} \delta \frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)}$$

- We now define the speed of the activated complex crossing the barrier top (gas collision). This is $\langle u_{\text{ac}} \rangle$, where $\langle u_{\text{ac}} \rangle = \nu_c \delta$ (the frequency \times distance).
- We have that

$$\langle u_{\text{ac}} \rangle = \int_0^\infty u f(u) du = \sqrt{\frac{m^\ddagger}{2\pi k_B T}} \int_0^\infty u e^{-m^\ddagger u^2 / 2k_B T} du = \sqrt{\frac{k_B T}{2\pi m^\ddagger}}$$

and the following

$$k = \frac{k_B T}{hc^\circ} \frac{(q_{\text{int}}^\ddagger/V)c^\circ}{(q_A/V)(q_B/V)} = \frac{k_B T}{hc^\circ} K_c^\ddagger$$

- We start at zero instead of $-\infty$ because we're only considering the forward direction of the reaction. If we did $-\infty$, we'd be accounting for the reverse reaction as well.
- Introducing $\Delta^\ddagger G^\circ = -RT \ln K_c^\ddagger = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$ yields the **Eyring equation**

$$k(T) = \frac{k_B T}{hc^\circ} e^{-\Delta^\ddagger G^\circ / RT} = \frac{k_B T}{hc^\circ} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT}$$

- We can relate the Eyring equation to the Arrhenius equation by differentiating the logarithm.

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_c^\ddagger}{dT} \qquad \frac{d \ln K_c}{dT} = \frac{\Delta U^\circ}{RT^2}$$

gives

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{\Delta^\ddagger U^\circ}{RT^2}$$

- This all serves to relate thermodynamics and kinetics.
- Additionally, since $\Delta^\ddagger H^\circ = \Delta^\ddagger U^\circ + \Delta^\ddagger PV = \Delta^\ddagger U^\circ + \Delta^\ddagger nRT$, we have that

$$\frac{d \ln k}{dT} = \frac{\Delta^\ddagger H^\circ + 2RT}{RT^2}$$

- Note that $\Delta n = -1$ for bimolecular gas phase reactions.
- $\Delta(PV)^\ddagger$ is the difference in the number of moles of gaseous products and reactants.
- $\Delta n^\ddagger = 0$: Unimolecular.
- $\Delta n^\ddagger = -1$: Bimolecular.
- $\Delta n^\ddagger = -2$: Trimolecular.
- Comparing with the Arrhenius $d \ln k / dT = E_a / RT^2$ gives

$$E_a = \Delta^\ddagger H^\circ + 2RT$$

- Substituting into the Eyring equation yields

$$k(T) = \frac{e^2 k_B T}{hc^\circ} e^{\Delta^\ddagger S^\circ / R} e^{-E_a / RT}$$

- Gas, uni: $E_a = \Delta H^\ddagger + RT$, $A = e k_B T / h \cdot e^{\Delta S^\ddagger / R}$.
- Gas, bi: $E_a = \Delta H^\ddagger + 2RT$, $A = e^2 k_B T / h c^\circ \cdot e^{\Delta S^\ddagger / R}$.
- Gas, tri: $E_a = \Delta H^\ddagger + 3RT$, $A = e^3 k_B T / h (c^\circ)^2 \cdot e^{\Delta S^\ddagger / R}$.
- Important things to memorize from TST.
 - The Eyring equation.
 - Don't worry about the partition function mathematics, but understand the dimensional analysis.
 - Know that we collapse two $k_B T$ terms together; one from q_{trans} and one from $\langle u_{\text{ac}} \rangle$.
- Consider cyclohexane conformations.
 - We have that

$$\Delta^\ddagger H^\circ = 31.38 \text{ kJ mol}^{-1} \qquad \Delta^\ddagger S^\circ = 16.74 \text{ J mol}^{-1} \text{ K}^{-1} \qquad T = 325 \text{ K}$$

- We want to know $\Delta^\ddagger G^\circ$.
- But by the definition of the Gibbs energy,

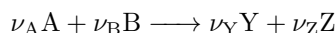
$$\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T \Delta^\ddagger S^\circ = 25.94 \text{ kJ mol}^{-1}$$

- It follows that

$$k = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT} = 4.59 \times 10^8 \text{ s}^{-1}$$

28.8 Chapter 28: Chemical Kinetics I — Rate Laws

- Whereas McQuarrie and Simon (1997) developed Quantum Mechanics from a set of simple postulates and Thermodynamics from the three laws, “the field of chemical kinetics has not yet matured to a point where a set of unifying principles has been identified” (McQuarrie & Simon, 1997, p. 1047).
 - There are many current theoretical models of kinetics, each of which has its merits and drawbacks.
 - Thus, right now, it is necessary to familiarize ourselves with numerous disparate ideas, as is common in developing fields of inquiry.
- **Rate law:** A differential equation describing the time-dependence of the reactant and product concentrations during a chemical reaction.
- Consider the general chemical reaction described by



- Since

$$n_A(t) = n_A(0) - \nu_A \xi(t) \quad n_B(t) = n_B(0) - \nu_B \xi(t) \quad n_Y(t) = n_Y(0) + \nu_Y \xi(t) \quad n_Z(t) = n_Z(0) + \nu_Z \xi(t)$$

we can describe the time-dependent change in the number of moles of each substance by taking a derivative with respect to t , as follows.

$$\frac{dn_A}{dt} = -\nu_A \frac{d\xi}{dt} \qquad \frac{dn_B}{dt} = -\nu_B \frac{d\xi}{dt} \qquad \frac{dn_Y}{dt} = \nu_Y \frac{d\xi}{dt} \qquad \frac{dn_Z}{dt} = \nu_Z \frac{d\xi}{dt}$$

- Since most experimental techniques measure concentration, it is convenient to divide the above equations by the total volume V on both sides to yield the following.

$$\frac{d[A]}{dt} = -\frac{\nu_A}{V} \frac{d\xi}{dt} \qquad \frac{d[B]}{dt} = -\frac{\nu_B}{V} \frac{d\xi}{dt} \qquad \frac{d[Y]}{dt} = \frac{\nu_Y}{V} \frac{d\xi}{dt} \qquad \frac{d[Z]}{dt} = \frac{\nu_Z}{V} \frac{d\xi}{dt}$$

- While each individual quantity above has its purpose, it is useful to define an overall **rate of reaction**.
- **Rate of reaction:** The following quantity. *Denoted by $v(t)$. Given by*

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

- Note that the rate of reaction is always positive (as long as the reaction proceeds only in the forward direction).
- **Rate law:** The relationship between $v(t)$ and the concentrations of the various reactants. *General form*

$$v(t) = k[A]^{m_A}[B]^{m_B} \dots$$
 - Some reactions (such as the $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ example from class) do not have conventional rate laws.
- **Rate constant:** The proportionality constant between the rate of reaction and the function of the concentrations of the chemical species involved in a rate law. *Denoted by k .*
 - The units of the rate constant depend on the form of the rate law.
- **Order** (of a reactant A): The power to which the concentration of a reactant is raised in a rate law. *Denoted by m_A .*
- **Overall order** (of a chemical reaction that obeys a general-form rate law): The sum of the orders of the reactants.
- We now discuss common methods for the experimental determination of a rate law.
- **Method of isolation:** The following procedure, which as described will determine m_B for a chemical reaction of the form introduced at the beginning of this section but can easily be adapted to determine m_A or be generalized to higher-order situations.

1. Introduce a large excess concentration of A into the initial reaction mixture. This excess will guarantee that $[A]$ remains essentially constant over the course of the reaction.
2. Combine $[A]^{m_A}$ and k into a new “rate constant” k' , reducing the rate law to the form

$$v = k'[B]^{m_B}$$

3. Determine m_B by measuring v as a function of $[B]$.
- Sometimes it is not possible to have one reactant or the other in excess.
 - As such, we need an alternate way to measure the rate.
 - We cannot directly measure $d[A]/dt$, but we can measure $\Delta[A]/\Delta t$ for small Δt and approximate these measurements as $d[A]/dt$.
 - This forms the basis for the **method of initial rates**.
 - **Method of initial rates:** The following procedure, which as described will determine m_B for a chemical reaction of the form introduced at the beginning of this section but can easily be adapted to determine m_A or be generalized to higher-order situations.
 1. Take two different measurements of the initial rate (from $t = 0$ to $t = t$). Let the initial concentration of A, $[A]_0$, be the same for each. However, for one, use $[B]_1$ for initial concentration of B, and for the other, use $[B]_2$.

2. Arranging everything into equations, we thus have

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

where we have used the subscripts 1 and 2 to denote the results of the different experiments and their corresponding initial concentrations of B.

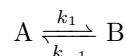
3. We may now solve for m_B by dividing the two equations, taking logarithms, and rearranging to the following.

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

- Both the method of isolation and the method of initial rates rely on the assumption that the reactants can be mixed, and then we can measure the rates.
 - However, for some very quick reactions, the time required to mix the reactants is long compared with the reaction itself.
 - For these cases, we need **relaxation methods**.

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- McQuarrie and Simon (1997) derives the first-order integrated rate law.
- To determine the rate constant of a first-order reaction from concentration vs. time data, plot the log of the concentration vs. time and perform a linear regression.
- **Half-life:** The length of time required for half of the reactant to disappear. *Denoted by $t_{1/2}$.*
- McQuarrie and Simon (1997) derives the half-life of a first-order reaction.
- “A particular rate law does not provide any information on the magnitude of the rate constant” (McQuarrie & Simon, 1997, p. 1057).
- McQuarrie and Simon (1997) derives the second-order integrated rate law.
- Similarly to first-order reactions, a plot of $1/[A]$ vs. time will yield a straight line with slope k and intercept $1/[A]_0$.
- To determine if a reaction is first- or second-order, we can make plots of $\ln[A]$ and $1/[A]$ vs. t and see which one is a straight line.
- McQuarrie and Simon (1997) derives the half-life of a second-order reaction.
- McQuarrie and Simon (1997) gives the integrated rate law for a reaction that is first-order in each reactant, and second-order overall.
- **Reversible** (reaction): A reaction that occurs in both directions.
- Consider the reversible reaction



- The kinetic condition for the above reversible reaction to be at equilibrium is

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

- **Dynamic equilibrium:** An equilibrium in which individual molecules of reactants and products continue interconverting but in such a way that there is no *net* change in either concentration.
- The rate law for the above reversible reaction is

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

- The first term accounts for the rate at which A reacts to form B.
- The second term accounts for the rate at which B reacts to form A.
- “The difference in sign of these two terms reflects that the forward reaction depletes the concentration of A and the back reaction increases the concentration of A with time” (McQuarrie & Simon, 1997, p. 1063).
- McQuarrie and Simon (1997) derives the integrated rate law corresponding to the above differential rate law and the case that $[B] = 0$.
- **Relaxation method:** A method of determining the rate law for a chemical reaction with half-life shorter than the mixing time, involving perturbing a chemical system at one equilibrium to a state that will require a new equilibrium by suddenly changing a condition.
 - Examples of conditions that can be changed are temperature, pressure, pH, and pOH.
- **Temperature-jump relaxation technique:** A relaxation method in which the temperature of the equilibrium reaction mixture is suddenly changed at constant pressure.
 - The change in temperature causes the chemical system to relax to a new equilibrium state that corresponds to the new temperature.
 - The rate constants for the forward and reverse reactions are related to the time required for the system to relax to its new equilibrium state.
- “Experimentally, the temperature of a solution can be increased by about 5 K in one microsecond by discharging a high-voltage capacitor through the reaction solution” (McQuarrie & Simon, 1997, p. 1067).
 - Since equilibrium constants depend exponentially on the inverse of the temperature ($\ln K_P = -\Delta_r G^\circ / RT$), such a perturbation can cause a large change in equilibrium conditions.
- As per the Van’t Hoff equation, the equilibrium concentration of B increases following the temperature jump if $\Delta_r H^\circ$ is positive and decreases if $\Delta_r H^\circ$ is negative.
 - If $\Delta_r H^\circ = 0$, then a temperature-jump relaxation experiment will not yield any useful data.
- Temperature-jump relaxation technique rate law derivation.
 - Suppose the initial temperature is T_1 and we increase the temperature to T_2 . Suppose furthermore that $\Delta_r H^\circ < 0$ so that the concentration of B decreases following the perturbation.
 - Let $[A]_{1,\text{eq}}, [B]_{1,\text{eq}}$ be the equilibrium concentrations of A and B, respectively, at T_1 . Let $[A]_{2,\text{eq}}, [B]_{2,\text{eq}}$ be the equilibrium concentrations of A and B, respectively, at T_2 . Let k_1, k_{-1} be the rate constants of the forward and reverse reactions, respectively, at T_2 . Let $[A], [B]$ be the concentrations of A and B, respectively, at some time T after the temperature jump. Let $\Delta[A], \Delta[B]$ be the differences in the concentrations of A and B, respectively, from equilibrium at time t .
 - As before, we begin from the fact that

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

- Notice how the sign convention follows from our hypothesis that $\Delta_r H^\circ < 0$.
- It follows by substituting

$$\Delta[A] = [A] - [A]_{2,\text{eq}} \qquad \Delta[B] = [B] - [B]_{2,\text{eq}}$$

into the above that

$$\begin{aligned} \frac{d}{dt}([B]_{2,\text{eq}} + \Delta[B]) &= k_1([A]_{2,\text{eq}} + \Delta[A]) - k_{-1}([B]_{2,\text{eq}} + \Delta[B]) \\ \frac{d\Delta[B]}{dt} &= k_1[A]_{2,\text{eq}} + k_1\Delta[A] - k_{-1}[B]_{2,\text{eq}} - k_{-1}\Delta[B] \end{aligned}$$

- The fact that $k_1[A]_{2,\text{eq}} = k_{-1}[B]_{2,\text{eq}}$ gives us

$$\frac{d\Delta[B]}{dt} = k_1\Delta[A] - k_{-1}\Delta[B]$$

- The fact that $\Delta[A] + \Delta[B] = 0$ gives us

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

- If $\Delta[B]_0 = [B]_{1,\text{eq}} - [B]_{2,\text{eq}}$, then it follows by integration that

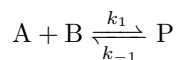
$$\int_{\Delta[B]_0}^{\Delta[B]} \frac{d\Delta[B]}{\Delta[B]} = \int_0^t -(k_1 + k_{-1}) dt$$

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

- **Relaxation time:** The reciprocal of the sum of the forward and reverse rate constants. *Denoted by τ . Units s. Given by*

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

- A measure of how long it takes for $\Delta[B]$ to decay to 1/e of its initial value.
- Temperature-jump relaxation technique rate law derivation for



- We have that

$$\frac{d[P]}{dt} = k_1[A][B] - k_{-1}[P]$$

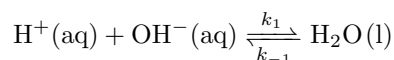
- If we define $\Delta[P]$ and the related relevant terms as in the above derivation, then we get

$$\begin{aligned} \frac{d}{dt}([P]_{2,\text{eq}} + \Delta[P]) &= k_1([A]_{2,\text{eq}} + \Delta[A])([B]_{2,\text{eq}} + \Delta[B]) - k_{-1}([P]_{2,\text{eq}} + \Delta[P]) \\ \frac{d\Delta[P]}{dt} &= k_1([A]_{2,\text{eq}}[B]_{2,\text{eq}} + [A]_{2,\text{eq}}\Delta[B] + \Delta[A][B]_{2,\text{eq}} + \Delta[A]\Delta[B]) - k_{-1}([P]_{2,\text{eq}} + \Delta[P]) \\ &= k_1([A]_{2,\text{eq}}\Delta[B] + \Delta[A][B]_{2,\text{eq}} + \Delta[A]\Delta[B]) - k_{-1}\Delta[P] \\ &= k_1(-[A]_{2,\text{eq}}\Delta[P] - \Delta[P][B]_{2,\text{eq}} + \Delta[P]^2) - k_{-1}\Delta[P] \\ &= -[k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}]\Delta[P] + O(\Delta[P]^2) \\ \Delta[P] &\approx \Delta[P]_0 e^{-t/\tau} \end{aligned}$$

where

$$\tau = \frac{1}{k_1([A]_{2,\text{eq}} + [B]_{2,\text{eq}}) + k_{-1}}$$

- Water dissociation, as per



- Time-dependent conductivity measurements following a temperature jump in water paired with the known equilibrium constant and the above derivation revealed a relaxation time that corresponds to one of the fastest second-order rate constants ever measured.
- Common temperature dependencies of chemical reactions.
 - As the temperature increases, the rate of reaction increases exponentially.

- The temperature dependence is exponential until a threshold temperature, and then increases extremely rapidly (i.e., the substance becomes explosive).
- The temperature dependence increases up until a threshold temperature, and then falls off rapidly (i.e., an enzyme-controlled reaction where the enzyme denatures at a certain temperature).
- In the first case (the most common), the temperature dependence of the rate constant is described approximately by the empirical equation

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

- Integrating yields the **Arrhenius equation**.
- **Arrhenius equation:** The following equation. *Given by*

$$k = Ae^{-E_a/RT}$$

- **Pre-exponential factor:** The constant A in the Arrhenius equation. *Denoted by A .*
- **Activation energy:** The constant E_a in the Arrhenius equation. *Denoted by E_a .*
- The magnitude of the temperature effect on reaction rates is much too large to be explained in terms of only a change in the translational energy of the reactions. Thus, a chemical reaction requires more than just a collision between reactants.
- **Reaction coordinate:** The unit along which a chemical reaction proceeds from reactant to product.
 - “Generally multidimensional, representing the bond lengths and bond angles associated with the chemical process” in question (McQuarrie & Simon, 1997, p. 1073).
 - A simple example, though, is that the I–I bond length serves as the reaction coordinate for the thermal dissociation of I_2 .
- The Arrhenius equation is imperfect, and many reactions obey equations of the form

$$k = aT^m e^{-E'/RT}$$

where a , E' , and m are temperature-independent constants.

- Note that

$$E_a = E' + mRT$$

$$A = aT^m e^m$$