CHEM 123: Summary of Important Concepts

Arranged by Hayden Scheiber - Available at ***bit.ly/2N4pXg8***

Thermodynamics

Equation/Concept	Info About Equation/Concept
System	The system is defined as a group of material and/or radiative contents. It's properties can be fully described by thermodynamic state variables.
Boundary	The boundary is the edge of a system. It may be a conceptual boundary or a real boundary.
Surroundings	The entire universe outside of the system and its boundary.
Isolated System	A system where neither energy nor mass can cross between the system and surroundings. The only truly isolated system is the entire universe, though we can produce approximately isolated systems (i.e. a well-insulated thermos).
Closed System	A system where energy can exchange with the environment, but mass cannot. A good example of a closed system would be a car's cooling system: when the car is on, heat moves from the radiator into the environment, but no coolant leaves the system.
Open System	A system where both energy and mass may freely exchange with the environment. Examples include open flask or cup of coffee.
State Variable	State variables are variables that describe the thermodynamic state (i.e. the conditions) of a system. They are only well-defined for systems in equilibrium. State variables **do not depend on the path taken** to get to a given thermodynamic state. Examples: temperature, pressure, internal energy, enthapy, Gibbs free energy, entropy, volume, density, mass, particle number, and concentration.
Path Variable	Path variables, unlike state variables, are non-zero only during a change in a system's thermodynamic state (i.e. when not at equilibrium). Path variables depend on the particular way in which a system evolves through time from one state to another. Heat and work are the only path variables used in this course.
Intensive Variable	These are variables that are independent of the system size. Examples include: temperature, energy density, pressure, density, concentration, and specific heat capacity. The ratio of two intensive variables is still intensive.
Extensive Variable	Extensive variables are variables that are proportional to the size of the system. If the system grows, then so do all extensive variables that describe the system. Examples include: internal energy, entropy, volume, mass, particle number, heat capacity. Dividing one extensive state variable by another will always produce an intensive variable because the system size dependence will cancel out.
Equation of State	At equilibrium, state variables are not independent from one another. An equation of state defines the particular relationship between state variables. Equations of state for real systems are often extremely complicated and may not have a closed form, but certain model systems can have fairly simple and useful relationships. For example, the ideal gas law is an equation of state that describes the relationship between state variables for a model gas system in which the particles of gas occupy zero volume (are point particles) and do not interact with each other. Although the ideal gas equation does not perfectly describe any gases in our universe, it becomes a very good approximation for dilute monatomic gases at high temperature.
Internal Energy (E or U)	Internal energy is the sum total of all forms of energy within a system. It includes all forms of potential energy, transnational energy, rotational energy, and vibrational energy. Generally, the total internal energy of a system is very difficult to measure, but changes in internal energy can be readily measured.
Heat (q)	Heat is the quantity of energy that transfers between the system and surroundings due to a difference in temperature. When heat is absorbed by the system, q is positive. When heat is removed from the system into the surroundings, q is negative. Heat only exists during a change in the system, it is a path variable.
Work (w)	Work is the energy transfer between system and surroundings due to a force applied over a distance. Work is associated with either an expansion (work done *by the system*, negative w) or a contraction (work done *on the system*, positive w) of the system. Work only exists during a change in the system, it is a path variable.

Equation/Concept	Info About Equation/Concept
Zeroth Law of Thermodynamics	*Two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another.* This law was only formulated after the first three laws of thermodynamics were already written down, but is more fundamental in nature than the other three.
$\Delta E = q + w$	This is the equation for the first law of thermodynamics. It states that the change in energy *of the system* is equal to the heat flow q into the system (positive q is heat flow *into* the system) plus the work done on the system w. Work done *on the system* corresponds to positive w. This is simply a statement of the conservation of energy and only applies *for a particular path.*
$\Delta E = q_V$	Change in internal energy when the volume of the system remains constant. The subscript simply indicates that the heat is exchanged at constant volume.
$đw = -P_{\text{ext}} dV$	The most general definition of the increment of work. This equation is for the *improper* increment of work done *on* the system. It is improper because work is a path variable, so the increment of work done is not an exact differential.
$w = -\int_{V_i}^{V_f} P_{\text{ext}} dV$	The definition of total work done on the system for a process. It is the integral from the initial volume to the final volume of the incremental amounts of work done along that path. This can be conceptualized as adding up the tiny increments of work $đw$ from the initial state to the final state. This is the most general expression for work done.
$w = -nRT \ln\left(\frac{V_f}{V_i}\right)$	The is the work done on an *ideal gas* expanding/contracting *reversibly and isothermally.* In this situation, $P_{ext} = P_{sys} = \frac{nRT}{V}$ at every point along the path, so the above integral can be solved analytically to obtain the result shown.
$w = -P_{\text{ext}} \Delta V$	This is the work done on a system with constant external pressure. This follows directly from the definition of total work done for the case in which P_{ext} is a constant.
Ideal Gas	An ideal gas is defined as a collection of point particles that do not interact with each other, but interact with the walls of their container elastically (i.e. energy and momentum is conserved for each collision). Ideal gas particles have masses, but the equation of state for ideal gases (ideal gas law) does not depend on particle mass. The internal energy of an ideal gas is $U = c_V nRT$, where c_V is the specific heat capacity at constant volume (approximately $\frac{3}{2}$ for a monatomic gas), n is the number of moles of gas, and T is the temperature. Hence the internal energy of an ideal gas only depends on T as long as the number of moles is held constant.
$PV = nRT$	This is the ideal gas law. It is the *equation of state* for a gas of point particles that do not interact with each other. P is the pressure of the system, V is the volume of the system, n is the number of moles of gas, R is the gas constant, and T is the absolute temperature. This equation works well to approximate the equation of state for real gases at low P and high T.
$P = \sum_i P_i = \sum_i \frac{n_i RT}{V}$	The equation of state for a mixture of ideal gases. P_i is called the **partial pressure** of gas i. The sum of the partial pressures for all gases in a mixture equals the total pressure. This is strictly true only for ideal gases, but is a good approximation otherwise.
$x_i = \frac{P_i}{P} = \frac{n_i}{n}$	For ideal gases only, the partial pressure for a component i in a mixture of ideal gases is proportional to the number of moles n. The partial pressure P_i divided by the total pressure is just $\frac{n_i}{n}$, known as the **mole fraction** x_i.
Isothermal Process	An isothermal process is a process that remains at a constant temperature along **the entire path** from its initial state to its final state.
Constant T Process	A process whose initial and final states have the same temperature, but may change temperature along the path between states.
Adiabatic Process	A process that occurs without exchange of heat at any point along the path. **Adiabatic walls** are system boundaries that do not allow exchange of heat. They are the walls of an isolated system. Inversely, **Diathermal walls** are boundaries that do allow heat exchange.
Reversible Process	An idealistic process that moves from one state to another while remaining in equilibrium with the surroundings along the entire path. Reversible processes would necessarily occur over an infinite amount of time, and so are not actually possible. A reversible process represents the upper limit on the possible work that can be extracted by an expanding gas, as well as the lower limit on the amount of work required to compress a gas. Reversible processes are called "reversible" because they require the same but opposite amount of work and heat to run backwards as forwards.

Equation/Concept	**Info About Equation/Concept**
Isobaric Process	An isobaric process is a process that occurs with no change in pressure along the entire path from initial to final state.
Isochoric Process	An isochoric process is a process that occurs with no change in volume along the entire path from initial to final state.
Heat Capacity C	Heat capacity is defined as the amount of energy required to raise the temperature of a system by 1 K. It is an **extensive** state variable, but may be made intensive by dividing by either the mass of the system or the number of moles.
$c_{sp} = \frac{C}{m}$	c_{sp} is called the specific heat capacity. It is an intensive state variable because it is the ratio of two extensive state variables. Here m is the mass of the system.
$c_m = \frac{C}{n}$	c_m is called the molar heat capacity. It is an intensive state variable because it is the ratio of two extensive state variables. Here n is the number of moles in the system.
$q = C\Delta T = mc_{sp}\Delta T = nc_m\Delta T$	The heat flow into the system is the product of the heat capacity C and the change in temperature $\Delta T = T_f - T_i$. Note that C is an extensive variable. This is only truly applicable for small changes in temperature, as C a temperature dependent state variable.
$H = E + PV$	Definition of enthalpy. Enthalpy is an extensive state variable which is most useful in constant pressure conditions and at equilibrium when $P = P_{ext}$. In this case, $\Delta H = q_p$ where q_p is the heat flow at constant pressure. Since pressure is often held constant in chemistry, enthalpy is a very useful state variable. The heat flow of a reaction is simply the change in enthalpy at constant pressure, so the enthalpy of formation for a reaction is quite easy to measure.
$\Delta H = \Delta E + P\Delta V$	The change in enthalpy for a constant pressure process. When a process results in $\Delta H < 0$ it is called **exothermic** and when a process results in $\Delta H > 0$ it is called **endothermic**. Reaction enthalpy alone is not enough to determine whether or not the process will proceed spontaneously.
Standard State	An arbitrary but agreed-up standard set of conditions for which many experimental state variables are measured: $P = 1\,\text{bar} \approx 1\,\text{atm}$ and either a pure substance or a 1 M solution. The standard state does not specify a temperature, but a separate term, standard temperature, is defined as $T = 273.15\,\text{K}$ while standard *ambient* temperature is defined as $T = 298.15\,\text{K}$.
ΔH_f°	ΔH_f° is the **standard enthalpy of formation**, sometimes called the **standard heat of formation**. It is defined as the change in enthalpy required to create **one mole** of a given substance at standard pressure (1 bar) starting from the compound's constituent elements in their standard states. The standard enthalpy of formation of any pure element in its standard state is then, by definition, $0\,\text{kJ}\,\text{mol}^{-1}$. Because ΔH_f° depends on temperature, the temperature must be defined, although it is often assumed to be 298.15 K.
$\Delta H^\circ_{\text{rxn}} = \sum_{\text{P}} \Delta H^\circ_{\text{f,P}} - \sum_{\text{R}} \Delta H^\circ_{\text{f,R}}$	Hess's Law. This law applies equally well to any state variable, such as total energy, entropy, etc. It is a reflection of the fact that the change in a state variable does not depend on the path taken. Here, P refers to products and R refers to reactants. Hess's law tells us that we can sum up as many processes as we wish in order to "build up" the value of an unknown state variable (such as enthalpy) from a set of known ones.
Entropy S	Entropy is an extensive state variable that can be thought of as a measure of the dispersal of energy within a system. Many people think of entropy as a measure of system disorder, but this is an imprecise and often wrong definition. Entropy is actually a measure of the number of possible microstates that would give rise to a given macrostate. For macrostates with a large number of potential microstates, entropy is high. From this we can see that very highly ordered macrostates will tend to (but not always) have relatively few microstates compatible with the macrostate, whereas disordered macrostates will have a high number of associated microstates.
General Cases of $\Delta S > 0$	Entropy generally increases when: temperature increases; pure liquids or solutions are formed from solids; the number of molecules of gas increases from a reaction; there is a decrease in pressure; and gases are formed from liquids.

Equation/Concept	**Info About Equation/Concept**
$\Delta S_{\text{Universe}} \geq 0$	The second law of thermodynamics. The equality is only satisfied for reversible processes or systems in equilibrium, for all non-reversible processes the inequality is true. Here $\Delta S_{Universe}$ is the change in entropy of the *entire universe* as a result of a process. Any process that proceeds must satisfy this inequality, but not every process that satisfies the inequality will proceed quickly (or at all). For example, the formation of graphite from diamond is favoured by entropy, but the reaction rate is essentially zero at ambient temperature.
$dS = \frac{đq_{\text{rev}}}{T_{\text{Surr}}}$	This is one definition of entropy. It is calculable only along a reversible path, but since once calculated the resulting ΔS applies to any path between the initial and final state.
$dS \geq \frac{đq}{T_{\text{Surr}}}$	The Clausius inequality. This is another expression of the second law of thermodynamics, and is only equal for a reversible process. This inequality states that for irreversible processes, it is not possible to pass heat between system and surroundings without increasing the entropy of the universe. Whichever body (system or surroundings) receives heat during a process must increase its entropy more than is lost by the body that is cooled.
$\Delta S = \frac{q_{\text{rev}}}{T}$	True for constant T, reversible heat exchange only. This equation is often used to measure changes in entropy by following a pseudo-reversible path.
$G = H - TS$	Definition of Gibbs free energy. Gibbs free energy is the criterion for determining if a reaction mixture will evolve towards reactants or products when the system is at constant P and T. Reactions in which $\Delta G < 0$ are said to be **exergonic**. Exergonic reactions are always spontaneous at constant T and P (but may not proceed quickly due to kinetic effects). Reactions with $\Delta G > 0$ are called **endergonic**, and are not spontaneous at constant T and P.
$\Delta G_{\text{System}} = -T\Delta S_{\text{Universe}}$	At **constant temperature and pressure**, the change in Gibbs free energy of the system tells us whether or not a process increases the entropy of the universe. Since T is always positive, and $\Delta S_{\text{Universe}}$ must be positive for a process to proceed, a negative ΔG corresponds to a process that *may* proceed spontaneously, as long as the activation barrier is much greater than $k_B T$.
$\begin{aligned} \Delta G^\circ &= -RT\ln(K) \\ &= \Delta H^\circ - T\Delta S^\circ \\ K &= \exp\left(\frac{-\Delta G^\circ}{RT}\right) \end{aligned}$	The standard Gibbs free energy. ΔG° is the Gibbs free energy change per mole of reaction of pure reactants to pure products at standard conditions (298 K, 1 atm, solutions at $1\,\text{mol}\,\text{L}^{-1}$ concentration, pure liquids and solids). K is the equilibrium constant for that reaction. $\Delta G^\circ < 0$ indicates products are favoured; $\Delta G^\circ > 0$ indicates reactants are favoured.
$S = k_B \ln(\Omega)$	The definition of entropy for an isolated system. Ω is the number of possible microstates and k_B is the Boltzmann constant, which is included to convert the units.
$\Delta G = \Delta H - T\Delta S$	The change in Gibbs free energy for a process done at constant temperature (although ΔH is most useful at constant P and T).
$\Delta G = \Delta G^\circ + RT\ln Q$	This equation can be used to predict the direction of a reaction. Q is called the "reaction quotient", and is the same as the equilibrium constant K, but calculated when a reaction has not yet reached equilibrium. $\Delta G < 0$ indicates that there are too many reactants and the reaction will favour products. $\Delta G > 0$ indicates that the reaction will proceed to the reactants side.
$K = \frac{[\text{Products}]}{[\text{Reactants}]}$	The definition of the equilibrium constant. Square brackets indicate concentrations, and the concentrations should be raised to the power of their stoichiometric coefficients.
$\Delta G = -T\Delta S_{\text{Universe}}$	This equation applies at constant temperature and pressure for a system. It is the reason that the change in Gibbs free energy is a measure of spontaneity under those conditions. $\Delta G < 0$ corresponds to an increase in the entropy of the universe when T and P are held fixed.
$\ln K = \frac{-\Delta H^\circ}{R}\frac{1}{T} + \frac{\Delta S^\circ}{R}$	The equation that describes a Van't Hoff plot: plot $\ln K$ vs $\frac{1}{T}$. The slope $m = \frac{-\Delta H^\circ}{R}$ and the y-intercept $b = \frac{\Delta S^\circ}{R}$. Using these plots assumes that the standard change in enthalpy and standard change in entropy are independent of T. This is only true for small changes in T. If the slope $m > 0$ then $\Delta H^\circ < 0$ and the reaction is exothermic. If $m < 0$ then $\Delta H^\circ > 0$ and the reaction is endothermic.
S°	The standard molar entropy. This is the absolute entropy of 1 mole of a substance in its standard state, usually measured at 298 K. By the third law, this is non-zero.

Equation/Concept	**Info About Equation/Concept**
$S_{0\,\text{K,perfect crystal}} = 0$	The third law of thermodynamics. Here $S_{0\,\text{K,perfect crystal}}$ refers to the entropy of a pure, perfectly crystalline solid at $0\,\text{K}$. The third law of thermodynamics gives us a reference point to define the zero of entropy. Basically, it states that there's only one possible microstate for a perfect crystal with no internal energy. The entropy for a system with only one microstate is $S = k_B \ln(1) = 0$.

For constant T and P processes, $\Delta G = \Delta H - T\Delta S$:

Sign of ΔH	Sign of ΔS	Sign of ΔG	Spontaneous?
+	+	+ (Low T) OR - (High T)	At High T
+	-	+	Never
-	+	-	Always
-	-	+ (High T) OR - (Low T)	At Low T

Thermodynamics of Acids and Bases

Equation/Concept	**Info About Equation/Concept**
Le Chatelier's Principle	A useful principle used to predict the response of equilibrium reactions to the application of some change to the system's equilibrium. If a change in pressure, temperature, volume, or concentration of a reactant is applied to a system in equilibrium, the equilibrium will respond by shifting so as to partly counteract the effect of the change.
$K_a = \frac{[H_3O^+][A^-]}{[AH]}$	Definition of the acid dissociation constant. This is simply the equilibrium constant for acid reactions. AH is an arbitrary acid and A^- is its conjugate base. Concentrations should all be raised to the power of their stoichiometric coefficients. Strong acids have very large K_b values ($K_a \gg 1$) while weak acids tend to have $K_a < 1$.
$K_b = \frac{[OH^-][BH^+]}{[B]}$	Definition of the base dissociation constant. This is simply the equilibrium constant for base reactions. B is an arbitrary base and BH^+ is its conjugate acid. Concentrations should all be raised to the power of their stoichiometric coefficients. Strong bases have very large K_b values ($K_b \gg 1$) while weak bases tend to have $K_b < 1$.
Strong Acids and Bases	Strong acids to know: HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$. Strong bases to know: $NaOH$, KOH, $Ca(OH)_2$. Strong acids and bases almost completely dissociate in solution, and thus have extremely high K_a and K_b values, respectively.
Buffer Solution	A solution containing an acid and its conjugate base in comparable concentrations ($10 \geq \frac{[Acid]}{[Base]} \geq 0.1$). Buffers resist large changes in pH brought on by addition of strong acids or bases by providing sources that neutralize both H^+ or OH^- in solution. Buffers always have $pH = pK_a \pm 1$ and $pOH = pK_b \pm 1$.
$K_W = K_a K_b = [H_3O^+][OH^-]$	Water self-dissociation constant. This is equal to 10^{-14} at $25\,°\text{C}$. It is the equilibrium constant for pure water undergoing dissociation. K_a and K_b refer to the acid and base dissociation constants of a **conjugate pair** in aqueous solution. The value of K_W increases with temperature.
$pH = -\log_{10}[H_3O^+]$	Definition of pH, pOH is defined similarly, where $[H_3O^+]$ is replaced by $[OH^-]$.
$pK_W = pK_a + pK_b = pH + pOH$	Equal to 14 at $25\,°\text{C}$. The water self-dissociation constants in terms of negative logs.
$[AH]_{\text{Buffer}} \approx 0.1[A^-]$ to $10[A^-]$	For effective buffers, the acid and conjugate base should be within 10 times concentration of each other.
$pH_{\text{Buffer}} \approx pK_a \pm 1$	A more succinct way of stating that buffers must be within 10 times concentration of each other.
$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right)$	The Henderson-Hasselbalch equation. Here AH and A^- are an acid base conjugate pair. This equation is useful in determining how the pH changes as a result of addition of an acid or base to a *buffer solution.* The equation implicitly assumes that the change in concentrations of the acid and conjugate base is negligible. This is only appropriate for solutions that begin as buffers and stay as buffers upon addition of some small amount of another acid or base.

Equation/Concept	Info About Equation/Concept
$\beta = \frac{\Delta n}{\Delta pH}$	β is the buffer Capacity: a measure of the efficiency of a buffer in resisting changes in pH. Buffer capacity is defined as the amount of a strong acid or a strong base that has to be added to 1 liter of a buffer to cause pH change of 1.0 pH unit. Here, Δn is the number of equivalents of strong acid/base added per liter of solution, and ΔpH is the resulting change in pH. The buffer capacity is maximized when the ratio of conjugate acid to conjugate base is 1:1.

Using ICE Tables: An Example

Calculate the new pH if 10.0 mL of 0.10 M HCl is added to the buffer made by mixing 25 mL of 1.0 M CH_3COOH and 25 mL of 0.50 M CH_3COONa. $K_a(CH_3COOH) = 1.8 \times 10^{-5}$

First step is to determine the initial number of moles of all reagents.

- HCl: $0.10\,\mathrm{mol\,L^{-1}} \times 0.010\,\mathrm{L} = 0.001\,\mathrm{mol}$
- CH_3COOH: $1.0\,\mathrm{mol\,L^{-1}} \times 0.025\,\mathrm{L} = 0.025\,\mathrm{mol}$
- CH_3COONa: $0.50\,\mathrm{mol\,L^{-1}} \times 0.025\,\mathrm{L} = 0.0125\,\mathrm{mol}$

Since HCl is a strong acid, we know it will react entirely in solution. It will react with any available weak bases and convert them into their conjugate acids. The base in this solution will be generated by the dissociation of CH_3COONa into CH_3COO^- (a weak base) and Na^+ (an nonreactive spectator ion). We can build an ICE (Initial-Change-End) table based on this. ICE tables may be used with number of moles or concentrations of reagents *using the total volume of the solution.* Here we will use the number of moles.

	HCl +	CH_3COO^- →	Cl^- +	CH_3COOH
Initial amount	0.001 mol	0.0125 mol	0 mol	0.025 mol
Change	−0.001 mol	−0.001 mol	+0.001 mol	+0.001 mol
Ending amount	0 mol	0.0115 mol	0.001 mol	0.026 mol

Now we should test whether or not the new solution forms a buffer or not. If $10 \geq \frac{[CH_3COOH]}{[CH_3COO^-]} \geq 0.1$, then the solution is a buffer. Since volumes cancel out, we can use the number of moles or the concentration.

- $\frac{[CH_3COOH]}{[CH_3COO^-]} = \frac{0.026\,\mathrm{mol}}{0.0115\,\mathrm{mol}} = 2.26.$

This is within acceptable bounds, and so the mixture is still considered a buffer solution after addition of the strong acid.

If it were not a buffer solution, then we would need to construct a second ICE table where the changes in concentration would be unknown, and solve for the unknown variable using the definition of K_a and its known value.

To calculate the pH of a buffer solution, we may use the Henderson-Hasselbalch equation. This equation only works for buffer solutions because it assumes that the concentrations of the acid and base conjugate pair do not change much from their initial concentrations (in this case, the concentrations after addition of the strong acid).

Notice that the volume dependence of the concentrations of acid and base in this equation cancel out. Therefore one may use either concentrations *or* number of moles in the second term of the equation.

$$\begin{aligned} pH &= pK_a + \log_{10}\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) \\ &= -\log_{10}\left(1.8 \times 10^{-5}\right) + \log_{10}\left(\frac{0.0115\,\mathrm{mol}}{0.026\,\mathrm{mol}}\right) \\ &= 4.39 \end{aligned}$$

For buffer solutions, the pH should always be within ±1 of the pK_a value, which in this case is $-\log(1.8 \times 10^{-5}) = 4.74$. This confirms that the solution is indeed a buffer, and can be used as a check to ensure your answer makes sense.

Derivation of the Henderson-Hasselbalch Equation for Buffers

We begin the derivation with an acid equilibrium reaction. The is just the acid dissociation reaction of a unspecified weak acid HA with water,

$$HA + H_2O \rightleftharpoons A^- + H_3O^+. \tag{1}$$

The ratio of products to reactants in this reaction defined by the equilibrium constant K_a (as long as T does not change). The definition of K_a is

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}. \tag{2}$$

Strictly speaking, the chemical activities of each species should be used, not their concentrations. In practice, concentrations are a good working approximation as long as the solutions are not highly concentrated, and therefore highly non-ideal. The next step is to take the base ten logarithm of each side to obtain

$$\log_{10}(K_a) = \log\left(\frac{[A^-][H_3O^+]}{[HA]}\right). \tag{3}$$

Using the multiplicative log law, $\log(a \times b) = \log(a) + \log(b)$ we can rearrange to yield

$$\log_{10}(K_a) = \log\left(\frac{[A^-]}{[HA]}\right) + \log([H_3O^+]) \tag{4}$$

$$-\log([H_3O^+]) = -\log_{10}(K_a) + \log\left(\frac{[A^-]}{[HA]}\right) \tag{5}$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{6}$$

The Henderson-Hasselbalch equation is just a rearranged version of the equation for K_a. Why is it so useful for buffer solutions in particular? Buffer solutions contain both acids and their conjugate bases in similar concentrations (within an order of magnitude of each other). An assumption that is often made using the Henderson-Hasselbalch equation is that the initial concentrations of the acid and conjugate base do not change appreciably when mixed in solution. This assumption is only accurate for buffer solutions that are not too dilute, as it implies that the dissociation of either side of the buffer is negligible compared with their initial concentrations.

Another approximation of the Henderson-Hasselbalch equation is that it does not take into account the effect of self-ionization of water on the pH of a solution. Most of the time this effect is negligible, but it becomes significant for very dilute (less than $1 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) solutions.

So the Henderson-Hasselbalch equation has only a fairly narrow range of applicability in the form commonly used. Too dilute, and the effects of ionization of the weak acid/base become apparent as well as the self-ionization of water. Too concentrated, and the concentrations of the species deviate too far from their activities to yield high accuracy.

Free Energy vs Reaction Progress

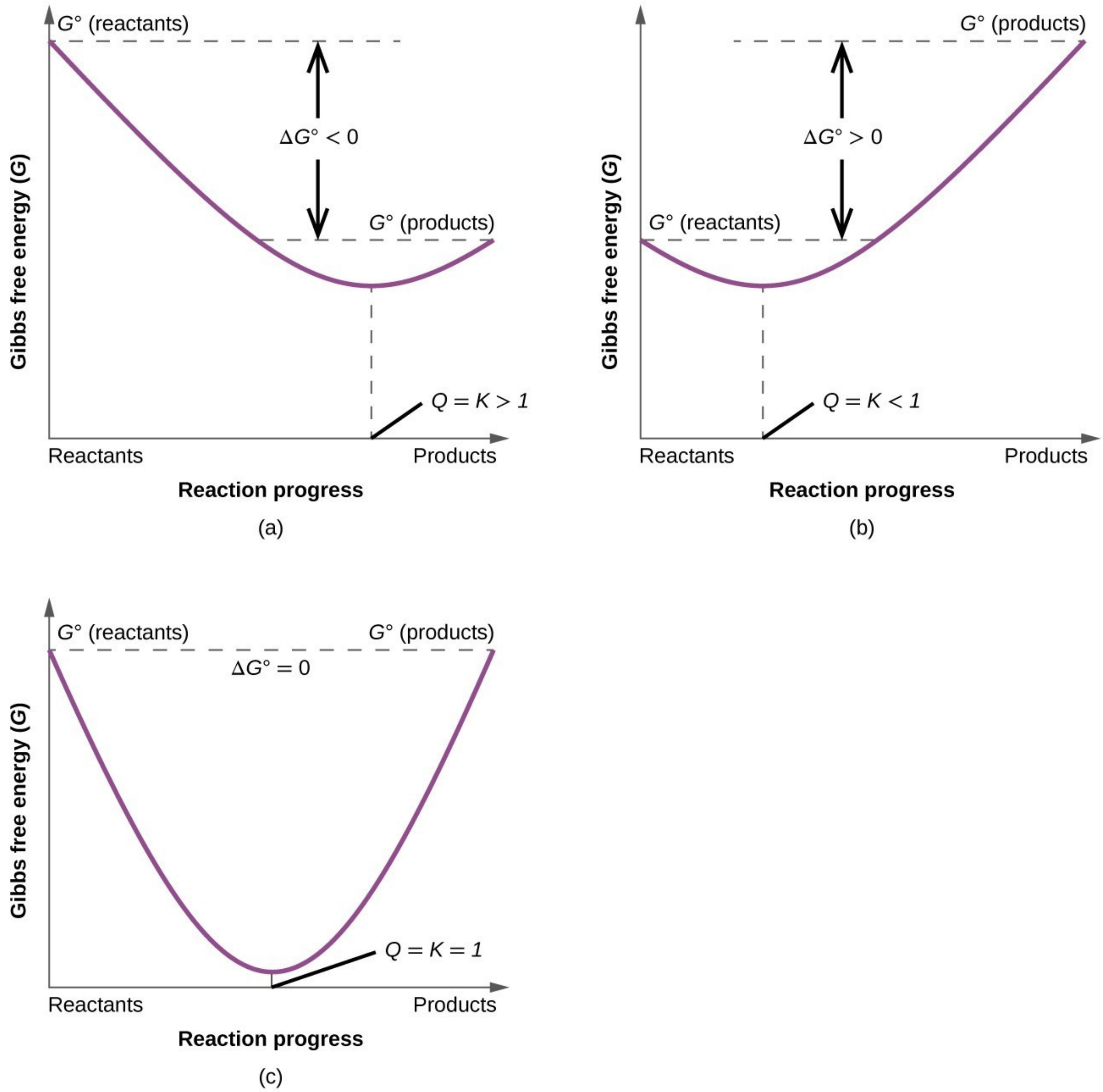


Figure 1: These useful figures[1] show the Gibbs free energy of a hypothetical reaction that goes from 100% pure reactants in their standard state on the left to 100% pure products in their standard state on the right. As the reaction mixture changes from 0% products to 100% products, the Gibbs free energy of the reaction mixture changes accordingly. The corresponding reaction progress at minimized standard Gibb's free energy represents the ratio of reactants to products at equilibrium, at standard pressure and the given temperature (usually 298 K). There are three possible cases: **(a)** G°(reactants) is higher than G°(products). In this case, we see that the ΔG° is negative, and at equilibrium there will be a greater proportion of products than reactants. **(b)** G°(products) is higher than G°(reactants). In this case, ΔG° is positive and the reaction mixture favours reactants at equilibrium. **(c)** G°(products) = G°(reactants), so that $\Delta G^\circ = 0$. This is an extremely unusual situation, but would result in an exactly equal ratio of products to reactants at equilibrium.

It should be emphasized that the plots on this page are **not** the same as plots for Gibbs free energy vs reaction coordinate. On the above plots, reaction progress represents the relative amount of reactants and products in a reaction mixture. It is inherently a bulk property of the mixture. Plots of Gibbs free energy vs **reaction coordinate** are different. Reaction coordinate is a more abstract idea that refers to the progress of a particular reagent or collection of reagents along what is considered to be the lowest energy reaction trajectory. In other words, the reaction coordinate represents the easiest pathway between a single molecule (or minimal group of molecules) of reactant to a single molecule (or minimal group of molecules) of product.

[1]Taken From: https://courses.lumenlearning.com/suny-mcc-chemistryformajors-2/chapter/free-energy/

Kinetics

Equation/Concept	Info About Equation/Concept
Factors That Increase Reaction Rates	1. Increase the temperature to increase the average kinetic energy per particle to overcome the transition state energy barrier. 2. Add a catalyst which lowers the transition state energy barrier of the reaction. 3. Increase the concentration of reactants (except for zero order reactions) allowing more collisions to occur per unit time.
$\Delta G^{\ddagger}$	The Gibbs free energy of activation. This is the free energy change required to reach the transition state, measured as the difference in Gibbs free energy between the transition state and the reactants.
Rate Determining Step	For a multi-step reaction, the rate determining step is the step with the highest Gibbs free energy barrier, $\Delta G^{\ddagger}$.
Elementary Reaction	A reaction that proceeds through only one step, has only one energy barrier, and one transition state. For a general elementary reaction $aA + bB \rightarrow cC$ the rate law is always Rate $= k[A]^a[B]^b$ where k is the rate constant.
Thermodynamically Controlled	When $\Delta G^{\ddagger}$ for both reactants and products is small compared with RT, then the energy barrier between reactants and products is easily overcome with the available thermal energy. Such a situation is said to be under thermodynamic control. Equilibrium is quickly established, and the final ratio of reactants or products can be predicted by the equilibrium constant K. Under thermodynamic control, the lowest Gibbs free energy species will be favoured.

Reaction Coordinate Diagrams

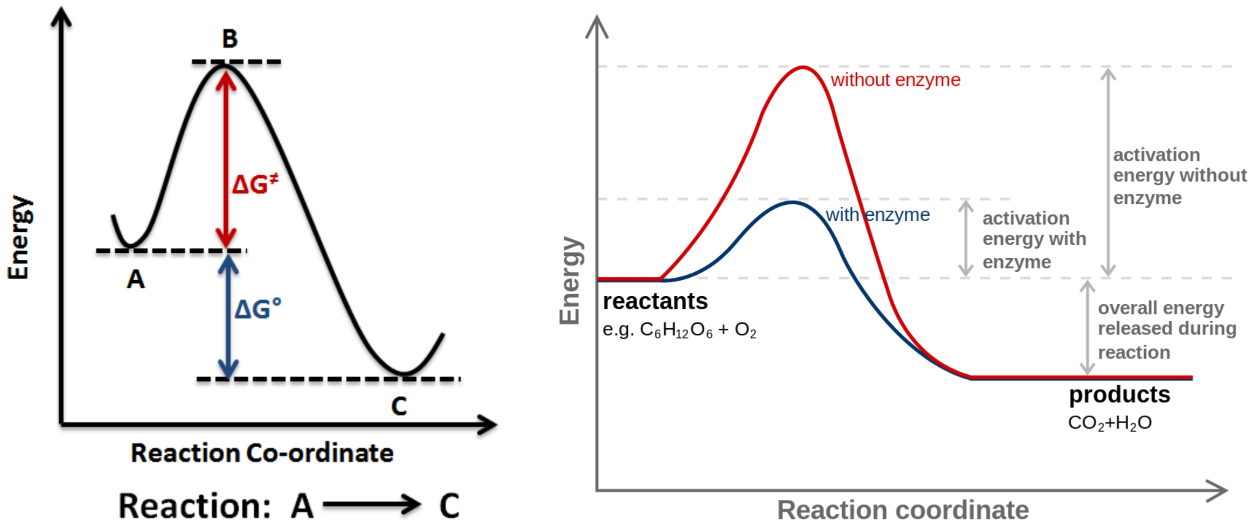


Figure 2: **(Left)** A diagram of Gibbs free energy vs reaction coordinate for an elementary reaction. In this context, the reaction coordinate refers to the point along the reaction pathway from reactant to product that requires the lowest raise in free energy. It is easy to imagine an multitude of potential pathways between a set of reactants and a set of products, but most of would be highly unlikely in reality. The reaction pathway that is most likely to occur is chosen, and its progress is delineated by the reaction coordinate. **(Right)** The effect of a biological catalyst (called an enzyme) on the reaction between glucose and oxygen. The catalyst does not change the free energy of the reactants or products, but lowers the energy of activation by stabilizing the transition state.[2]

As one moves along the reaction coordinate between reactant and product, there is always a potential energy barrier called the **energy of activation**. If there were no such barrier, the reactants could not exist for more than the length of a molecular vibration (approximately 1×10^{-10} s) without decaying into the products. The highest point along the energy barrier is called the **transition state** and is usually marked with the double dagger symbol (‡). Transition states are not isolable species, they only exist for around the length of time of a molecular vibration before either decaying to products or back to reactants. Transition states generally look intermediate between reactants and products, but tend to be more similar in structure to the side with a smaller gap in free energy (reactants in this case). This principle is known as Hammond's postulate.

[2]Left: http://www.wikiwand.com/en/Energy_profile_(chemistry) Right: https://en.wikipedia.org/wiki/Reaction_coordinate

Equation/Concept	**Info About Equation/Concept**
Kinetically Controlled	When $\Delta G^{\ddagger} \gg RT$ with respect to the reactants, products, or both, then the average molecule does not have enough kinetic energy to overcome the activation barrier and equilibrium cannot be quickly established. Such reactions are said to be under kinetic control, and may proceed very slowly or not at all in one or both directions. Kinetic control can be used to force a reaction to produce a side different product than would otherwise be favoured under thermodynamic control.
Reaction Mechanism	A detailed description of the steps leading from reactants to products. A reaction mechanism may be one elementary step or a series of elementary steps.
Transition state	The point(s) along a particular reaction pathway that are peaks in the Gibbs free energy.
Overall Reaction	The entire reaction from initial reactants to final products, as opposed to the elementary reactions that make up the reaction.
Catalyst	Any reagent that is used in a reaction but later regenerated *and* lowers the activation energy of a reaction. Living creatures contain countless protein-based catalysts called **enzymes** that allow fine control of the chemistry of their internal systems.
Zero Order Reactions	These types of elementary reactions do not depend on the concentration of the reactants. Such reactions usually depend on some catalyst, which is limiting the rate of the reaction. Zero order kinetics are an artifact of the reaction conditions, and will collapse to higher order kinetics when the concentration of reactants becomes low enough to limit the rate of reaction (instead of the catalyst).
$\text{Rate} = -\frac{b}{a}\frac{d[A]}{dt} = k$	The zero order differential rate law for a general reaction $a[A] \to b[B]$. This is used to calculate the rate constant k. $[A]$ is the concentration of reactants and a is its stoichiometric coefficient. b is the stoichiometric coefficient of the products. The "Rate" here is always the rate of product formation. Often times this equation will be written without the factor of $\frac{b}{a}$, with $k' = \frac{a}{b}k$.
$[A](t) = -kt + [A]_0$	This is the integrated rate law for a zero order reaction, note that the rate constant here is really $\frac{a}{b}k$. This equation will provide the concentration of the reactants as a function of time. Plots of $[A]$ vs t will be linear for zero order reactions, with a slope of $-k$ and a y-intercept of $[A]_0$.
$t_{\frac{1}{2}} = \frac{[A]_0}{2k}$	The half-life of a zero order reaction. This depends on the initial concentration of reactants.
First Order Reactions	These types of reactions depend on the concentration of only one reactant, which a stoichiometric coefficient of 1. For example, the elementary reaction $A \to bB$.
$\text{Rate} = -b\frac{[A]}{dt} = k[A]$	The differential rate law for a first order reaction $A \to bB$. Often the rate constant k will include the factor of $\frac{1}{b}$.
$[A](t) = [A]_0 e^{-kt}$	The integrated rate law for first order reactions. This can also be written as $\ln[A] = -kt + \ln[A]_0$. This equation can be used to determine the concentration of reactants as a function of time. Plots of $\ln[A]$ vs t will be linear for first order reactions, with a slope of $-k$ and a y-intercept of $\ln[A]_0$.
$t_{\frac{1}{2}} = \frac{\ln 2}{k}$	The half-life for a first order reaction. This does not depend on the initial concentration of the reactants.
Second Order Reactions	These types of reactions depend on the concentration of one reactant with a stoichiometric coefficient of 2, or on the concentration of two reactants. For example, the elementary reaction $2A \to bB$.
$\text{Rate} = -\frac{b}{2}\frac{[A]}{dt} = k[A]^2$	The differential rate law for a first order reaction $A \to bB$. Often the rate constant k will include the factor of $\frac{2}{b}$.
$\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$	The integrated rate law for second order reactions. This equation can be used to determine the concentration of reactants as a function of time. Plots of $\frac{1}{[A]}$ vs t will be linear for second order reactions, with a slope of k and a y-intercept of $\frac{1}{[A]_0}$.
$t_{\frac{1}{2}} = \frac{1}{[A]_0 k}$	The half-life for a second order reaction. This depends on the initial concentration of the reactants.
$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$	The Eyring equation. This applies only to elementary reactions, and can be used to determine the Gibbs free energy of activation. k_B is the Boltzmann constant, which is just $\frac{R}{N_A}$ where N_A is Avagadro's number. This reaction comes about by assuming that formation of the transition state is kinetically controlled (i.e. is in equilibrium) but the formation of products is thermodynamically controlled (i.e. is irreversible).

Equation/Concept	Info About Equation/Concept
$k = Ae^{-\frac{E_a}{RT}}$	The Arrhenius equation. This applies to any reaction and describes the effect of temperature on the rate of reaction. A is the pre-exponential factor, and is usually assumed to be temperature independent over small changes in temperature; it describes the frequency of collisions that occur with the correct orientation (different for each reaction). E_a is the activation energy per mole, and is the minimum energy required to overcome the energy barrier for reaction. RT is the average thermal energy per mole. This equation is sometimes written $\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$ so that plots of $\ln k$ vs $\frac{1}{T}$ are linear with a slope of $-\frac{E_a}{R}$ and a y-intercept of $\ln A$.
$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right)$	The linear form of the Eyring equation. Plots of $\ln\left(\frac{k}{T}\right)$ vs $\frac{1}{T}$ will be linear. The slope will be $-\frac{\Delta H^{\ddagger}}{R}$ and the y-intercept will be $\frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right)$.
Reaction Intermediates	These are species that are generated in one step of a reaction and consumed in a subsequent step.
$\frac{d[\text{intermediates}]}{dt} = 0$	This is the steady-state approximation. Useful for reactions where the rate determining step is the production of an intermediate. This often greatly simplifies the rate laws for multi-step reactions.
$V_0 = \frac{V_{\max}[S]}{K_m+[S]}$	The Michaelis-Menton equation. Describes the kinetics of the enzyme equilibrium reaction $E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_{\text{cat}}} E + P$. Here, $K_M = \frac{[E][S]}{[ES]} = \frac{k_{-1}+k_{cat}}{k_1}$ is the equilibrium constant for the enzyme-substrate binding; V_0 is the rate of product formation; $V_{\max} = k_{\text{cat}}[E]_{\text{total}}$ is the reaction rate when all available enzymes are saturated. Derivation of this equation involves the steady state approximation $\frac{d[ES]}{dt} = 0$. Notice that in the limit where the concentration of substrate is large compared to that of the enzyme, $K_M \ll [S]$ such that $K_M + [S] \approx [S]$ and $V_0 \approx V_{\max}$. In the limit of very low substrate concentration, $K_M \gg [S]$ such that $K_M + [S] \approx K_M$ and the kinetics become first order with respect to $[S]$.

Free Energy vs Reaction Progress

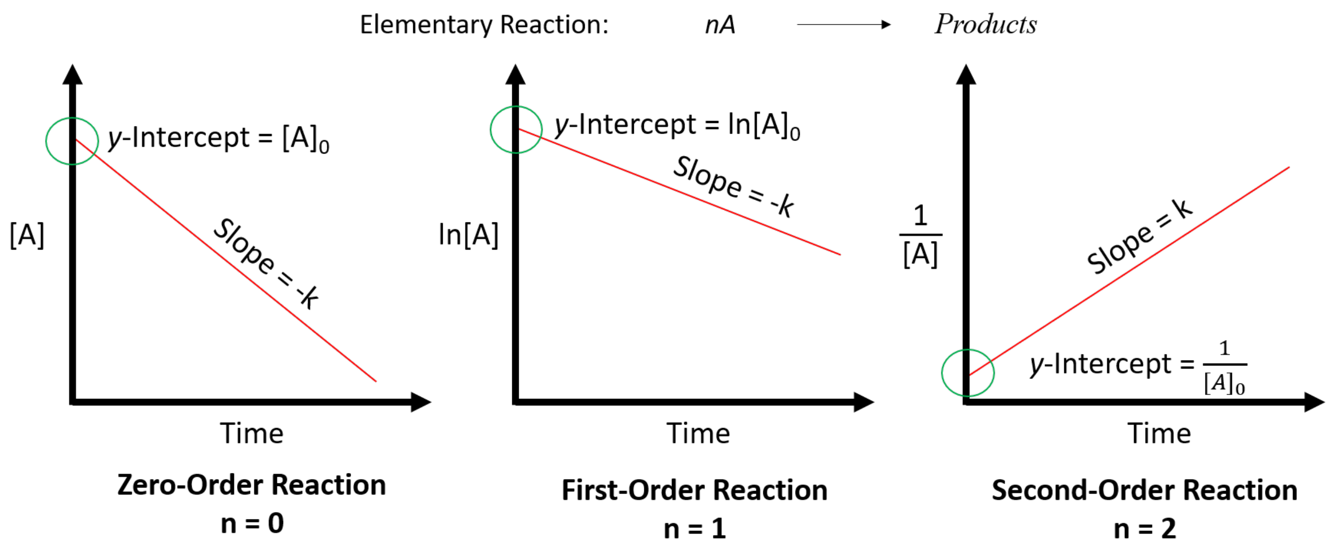


Figure 3: How we can use plots of concentration vs time to determine the order of a reaction with respect to a particular reactant. Only one of the above plots should be linear with respect to a particular reactant involved in a reaction. Find the linear plot to determine the reaction order. The reaction order is *also* the stoichiometric coefficient if the reaction is elementary.

Derivation of the Michaelis-Menton Equation

The Michaelis-Menton equation describes the kinetics of a biological catalyst E (called an enzyme) undergoing the following set of linked reactions:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_{cat}} E + P \tag{7}$$

- E is the enzyme
- S is the substrate
- ES is the enzyme-substrate bonded complex
- P is the product
- k_1, k_{-1}, and k_{cat} are the rate constants for the three involved reactions.

We make the assumption that the reaction $E + P \to ES$ does not appreciably occur, and can therefore be ignored. This is a common situation for many biological enzymes under normal physiological conditions. Each of the reactions in equation 7 is an elementary reaction. Therefore, the rate of formation of ES is simply

$$\text{Rate}_{ES} = k_1[E][S]. \tag{8}$$

The rate of breakdown of ES is more complicated because it depends on two separate elementary reactions,

$$\text{Rate}_{-ES} = k_{-1}[ES] + k_{cat}[ES] = (k_{-1} + k_{cat})\,[ES]. \tag{9}$$

Now we make the steady-state approximation with regards to the concentration of ES. That is,

$$\frac{d[ES]}{dt} = 0. \tag{10}$$

The only way for the concentration of ES to remain constant is if the rate of formation for ES equals the rate of breakdown, i.e. $\text{Rate}_{ES} = \text{Rate}_{-ES}$. Therefore, under the steady-state approximation we can set equations 8 and 9 equal to obtain

$$\begin{aligned} k_1[E][S] &= (k_{-1} + k_{cat})\,[ES] \\ \frac{[E][S]}{[ES]} &= \frac{k_{-1} + k_{cat}}{k_1} \equiv k_M. \end{aligned} \tag{11}$$

Here we have defined a new quantity called the Michaelis constant, k_M. The rate of product formation V_0 for the reaction described by 7 can be written as

$$V_0 = k_{cat}[ES]. \tag{12}$$

We now define a new quantity, $[E]_T = [E] + [ES]$ which is just the total concentration of free and bound enzyme. Rearranging gives us $[E] = [E]_T - [ES]$. Plugging this into equation 11 yields

$$\begin{aligned} k_M &= \frac{([E]_T - [ES])\,[S]}{[ES]} \\ k_M[ES] &= [E]_T[S] - [ES][S] \\ [ES]\,(k_M + [S]) &= [E]_T[S] \\ [ES] &= \frac{[E]_T[S]}{k_M + [S]}. \end{aligned} \tag{13}$$

Equation 13 is the expression for the enzyme-substrate complex under the steady-state approximation in terms of the easier-to-measure quantities $[E]_T$ and $[S]$. We now plug equation 13 back into equation 12 to get an expression for the rate of product formation in terms of these quantities,

$$V_0 = \frac{k_{cat}[E]_T[S]}{k_M + [S]}. \tag{14}$$

It is common to define $V_{max} \equiv k_{cat}[E]_T$ as the maximum possible rate of reaction for a given total concentration of enzyme, so equation 14 becomes

$$V_0 = \frac{V_{max}[S]}{k_M + [S]}. \tag{15}$$

This is the Michaelis-Menton equation in its common form.

The Michaelis-Menton equation has two interesting limiting behaviours. The first limit is when there is very little substrate, such that $[S] \ll [E]_T$. In this limit, $[E]$ will be very large and $[ES]$ will be very small such that

$$k_M + [S] = \frac{[E][S]}{[ES]} + [S] \approx \frac{[E][S]}{[ES]} = k_M. \tag{16}$$

This gives us the limiting behaviour

$$V_0 \approx \frac{V_{max}}{k_M}[S] \quad \text{if} \quad [S] \ll [E]_T. \tag{17}$$

which looks like first order kinetics for $[S]$ with a rate constant of $\frac{V_{max}}{k_M}$. The second limit occurs when there is a great excess of substrate such that $[S] \gg [E]_T$. In this case, $[E]_T \approx [ES]$ such that $k_M + [S] \approx [S]$ leading to

$$V_0 \approx V_{max} = k_{cat}[E]_T \quad \text{if} \quad [S] \gg [E]_T. \tag{18}$$

This looks like first order kinetics with respect to the total concentration of enzyme, as one might expect.

IUPAC/Common Organic Nomenclature Notes

Equation/Concept	**Info About Equation/Concept**
Principal Functional Group	• The principal functional group is used to define the class the compound belongs to e.g. an alcohol is ROH • The principal functional group is the highest priority functional group, as determined from the order in figure 4. • The principal functional group is usually given the lowest locant possible.
Longest chain	• The longest continuous chain **containing the principal functional group** defines the root name. • Other groups attached to this chain are called **substituents**. • If there are two chains of equal length, then the choice that gives the simplest substituents is chosen.
Numbering	• The numbers that define the positions of the principal functional group and substituents are called **locants**. • Compounds are numbered from one end of the longest continuous chain containing the principal functional group. • The locants are assigned such that the principal functional group gets the lowest possible locant. • If this results in a "tie" then the first point of difference rule is applied so that the first time a difference in numbering occurs, then the method that gives the lower number at this first difference is used. • In the event that there is no first point of difference then alphabetization is used.

Equation/Concept	**Info About Equation/Concept**
Suffix vs Prefix	The highest priority functional group is given the suffix, all other lower priority functional groups are named with prefixes. The molecule is then named as (substituents in alphabetical order)(longest carbon chain)(suffix of highest priority group).
Esters	• If the ester is the highest priority functional group, assign the alpha carbon (the carboxyl carbon) to number 1. • Name the group of the ester that does not contain the carbonyl as if it were a substituent group. Place the name of this substituent group in front. Name the primary chain as normal, but add "-oate" to the end (eg: ethyl methanoate).
Ethers	• Determine which side of the ether is the higher priority side: the shorter carbon chain becomes the "substituent" chain. • Name the shorter chain as normal, and then the "-oxy" suffix to the end. Place this name in front. • The higher priority chain is then named as normal under IUPAC rules, with no suffix.
Sulfides	• Determine which side of the sulfide is the higher priority side: the shorter carbon chain becomes the "substituent" chain. • Name the shorter chain as normal, and then the "-thio" suffix to the end. Place this name in front. • The higher priority chain is then named as normal under IUPAC rules, with no suffix.
Acyl Halides (Acid Halides)	• These functional groups have higher priority than amides, but lower than carboxylic esters. • Name it as if it were a carboxylic acid, but remove the "-oic acid" suffix. • Add the suffix "-oyl [hal]-ide" where "[hal]-ide" is replaced by the halogen in question (one of fluoride, chloride, bromide, or iodide).
Carboxylic Anhydrides	• These functional groups have higher priority than esters, but lower priority than carboxylic acids. • Name each side of the double carboxylic ester linkage separately, followed by the "-oic" suffix. • Alphabetically arrange them, separated by spaces, followed by the word "anhydride" (e.g. ethanoic propanoic anhydride).
n- Prefix	This (common name) prefix is occasionally used when all carbons in the molecule form a continuous unbranched chain (short for *normal*).
iso- Prefix	This (common name) prefix is used when all carbons for a continuous chain except for one methyl group attached to the second carbon. The 2-methyl group is included in the total number of carbon atoms used to determine the root name (e.g. isopentane has five carbons total, but the longest chain is only four).
sec- Prefix	This (common name) prefix is used to label functional groups attached to a **secondary carbon** (a carbon atom bonded to two other carbon atoms).
tert- Prefix	This (common name) prefix is used to label functional groups attached to a **tertiary carbon** (a carbon atom bonded to three other carbon atoms).

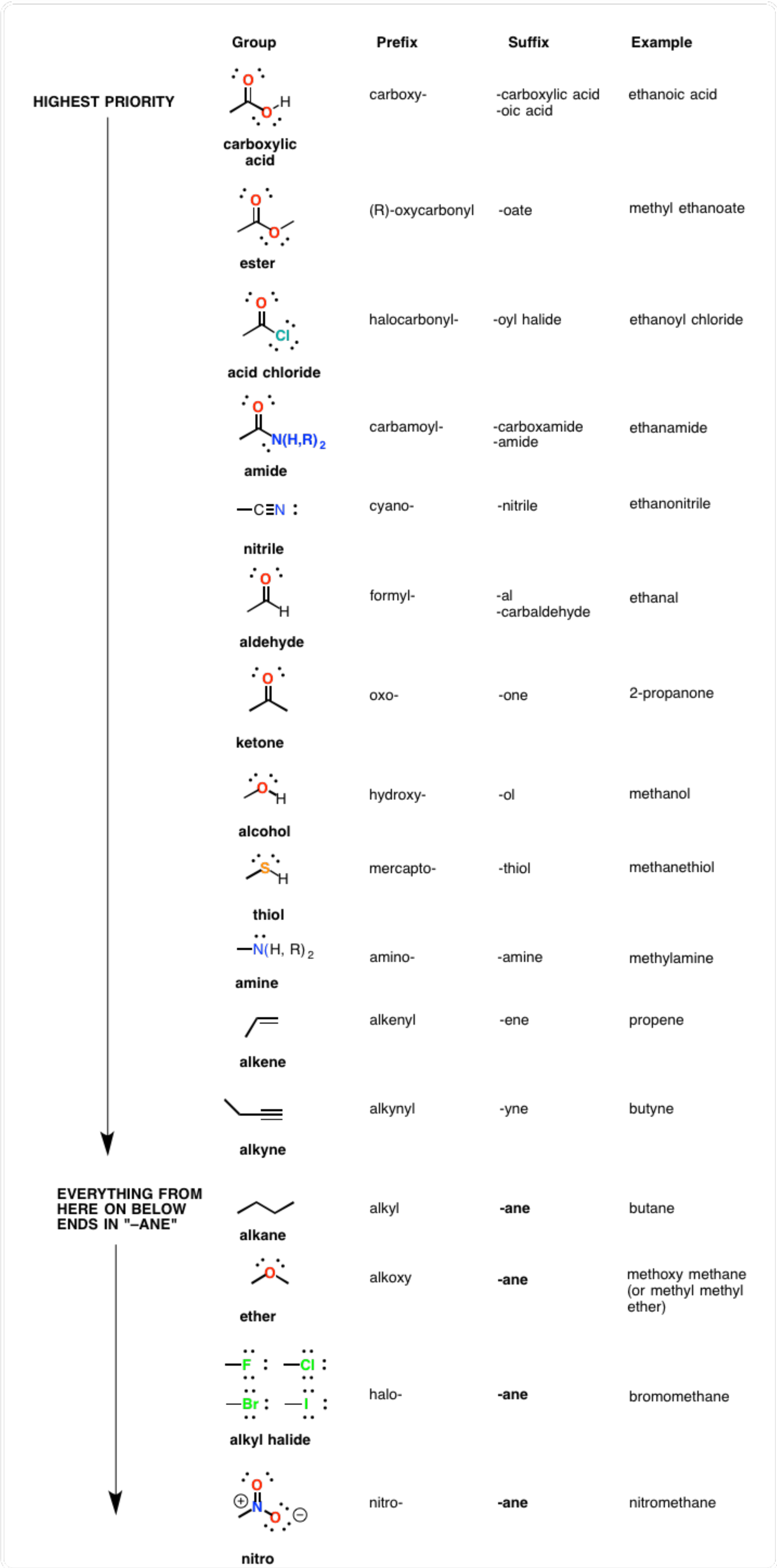
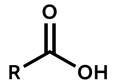
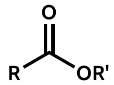
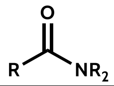
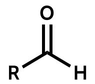
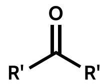


Figure 4: Summary of the IUPAC priority system for organic chemistry nomenclature.[3]

[3]https://www.masterorganicchemistry.com/2011/02/14/table-of-functional-group-priorities-for-nomenclature/

Organic Nomenclature Guide

Functional Groups (in order of decreasing priority)

Functional group	Formula	Shorthand	Principle name	Substituent name
Carboxylic acids		R-COOH	-oic acid	carboxy
Esters		R-COOR’	-oate	(R)oxycarbonyl
Amides		$R-CONR_2$	-amide	amido
Nitriles		R’-CN	-nitrile	cyano
Aldehydes		R-CHO	-al	oxo
Ketones		R’-CO-R’	-one	oxo
Alcohols	R’-OH		-ol	hydroxy
Thiols	R’-SH		-thiol	sulfanyl
Amines	$R'-NR_2$		-amine	amino
Hydrocarbons	R’-H		-e	(R)yl
Ethers	R’-O-R’		-ether	(R)oxy
Sulfides	R’-S-R’		-sulfide	(R)ylsulfanyl
Halides	R’-X (X=F, Cl, Br, I)		-(hal)ide (e.g. bromide)	(hal)o (e.g. fluoro)

Note: R=saturated C/alkyl or H; R’=saturated C/alkyl

Prefixes 1 (parent/substituent length)

R (# of carbons)	Prefix
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-

Infixes

Nature of C-C bonds	Infix
Single bond(s)	-an-
Double bond(s)	-en-
Triple bond(s)	-yn-

Prefixes 2 (multiple substituents/infixes)

# of repeated elements	Infix
2	di-
3	tri-
4	tetra-
5	penta-

IUPAC Nomenclature Rules

1. Identify the highest priority functional group and corresponding suffix.
2. Identify the parent chain (longest carbon chain that includes (if C-containing) or is directly attached to (if non-C-containing) the highest priority functional group) and corresponding prefix.
3. Identify the infix based on the nature of the C-C bonds in the parent chain (single/double/triple)
4. Number the parent chain from end to end, giving the lowest # to (1) the highest priority functional group; (2) multiple bonds; (3) substituents closest to the end; (4) groups that come first alphabetically
5. Identify the position and name of each substituent.
6. If two or more substituents are present on the same carbon atom, use the same number twice.
7. If a substituent group or infix appears more than once, use the prefixes: di, tri, tetra, penta, hexa etc.
8. List the substituents alphabetically at the beginning of the name (use the root names from rule 5, not the prefixes from rule 7 to alphabetize).
9. Numbers are separated from letters by dashes (-). Multiple numbers are separated by commas (,).

Organic Chemistry: Bonding and Bonding Theories

Equation/Concept	Info About Equation/Concept
Formal Charge	A book keeping device defined as: (Valence electrons) - (Lone Pair electrons) - $\frac{1}{2}$(Bonding electrons). The sum of all formal charges on a molecule always equals the total charge of the molecule.
Bond Dipole Moment (μ)	The product of a bond length and the difference in charge between each end. Bond dipoles are vectors, which have a magnitude and direction. The direction is always from the positive end of a bond to the negative end. The dipole moment of a perfectly covalent bond is zero.
Total Dipole Moment	The vector sum of all bond dipole moments is the total dipole moment of a molecule. The total dipole moment determines how polar a species is, which affects many of its physical and chemical properties.
Electronegativity	A measure of the tendency of an atom to attract electrons to itself. More electronegative atoms have lower energy frontier orbitals than less electronegative atoms. Electronegativity increases $\rightarrow$ and $\uparrow$ across the periodic table (see appendix). Electronegativity is usually quantified with the Pauling scale, which ranges from 0.7 to 4.0.
Non-Polar Covalent Bond	A bond between two atoms of the same or very similar electronegativity which has no (or a very small) dipole moment. Non-polar covalent bonds hold two atoms together through the mutual attraction of the bonding electrons, which are shared equally.
Polar Covalent Bond	A covalent bond between two atoms of moderately dissimilar electronegativity. Bonding electrons are shared, but the atom with higher electronegativity attracts more electron density towards itself than the atom with lower electronegativity. Thus, polar covalent bonds have moderate bond dipole moments.
Ionic Bond	A bond between two atoms with very disparate electronegativities where electrons are not shared. The bond forms due to electrostatic forces between two oppositely charged species, one of which has lost its electron to the other.
Lewis Theory	The simplest bonding theory. Non-bonding valence electrons are represented by dots (e.g. H·) and bonding electrons are represented by lines (e.g. H—H). Lewis theory works well for connectivity, but does not provide the correct molecular geometry.
VSEPR Theory	Valence Shell Electron Pair Repulsion Theory. Is able to predict molecular geometry by assuming freely movable substituents take on the lowest energy angular arrangement around a central atom. Does not predict molecular orbitals, and so cannot be used to predict reactivity.
Valence Bond Theory (VBT)	VBT is a simplified version of molecular orbital theory, which only involves the valence electrons. Predicts hybridization and good approximations for orbitals in organic molecules.
Molecular Orbital (MO) Theory	MO theory produces accurate molecular orbitals which correctly predict reactivity. Becomes extremely complicated for large molecules, so approximate theories are used.
Frontier MO theory	Frontier MO theory remixes the hybrid orbitals generated by VBT using the same method as MO theory.

Organic Chemistry: Reactivity and Acid-Base Chemistry

Equation/Concept	Info About Equation/Concept
Resonance	When two or more Lewis dot formulae for the same arrangement of atoms are necessary to fully describe the bonding in a molecule or atom, we call these structures resonance forms and connect them with resonance arrows: $\leftrightarrow$. Resonance is an artifact of the inaccuracies inherent in Lewis theory, which do not allow for partial bonding and electron delocalization to be shown from a single structure. In reality, the true structure is a weighted sum of all resonance structures, whose weights are determined by the relative stability of each resonance form. Resonance forms allow the movement of electrons through the π-system only. Additional reasonable resonance structures always work to lower the energy of the overall structure. Electrons flow form source (δ^-, -) to sink (δ^+, +). Resonance motifs: $\pi - \sigma - \pi$; $\pi - \sigma -$ charge; $\pi - \sigma -$ lone pair.

Equation/Concept	**Info About Equation/Concept**
Nucleophile	An electron-rich species that "seeks" positive charge to react with. Bases are often (but not always) good nucleophiles (counter example: extremely bulky bases are not good nucleophiles due to steric hindrance). Anions are usually good nucleophiles.
Electrophile	An electron-deficient species that "seeks" negative charge to react with. Positive or partially positive charged species often make good electrophiles. Acids are usually (but not always) good electrophiles.
$\mathbf{pK_a}$	A measure of acid strength. Lower pK_a means stronger acid. Higher pK_a means stronger conjugate base. A stronger acid is better at donating protons, while a stronger base is better at accepting protons.
Strong Acids and Bases	These are unstable species, their conjugates will be much more stable and hence highly favoured at equilibrium.
Electronegativity of Identical Atoms	Electronegativity increases with increasing s character, as s-orbitals are lower in energy. Therefore, for the same atomic species, the order of electronegativity is: sp > sp^2 > sp^3 > sp^3d > etc.
Position of Equilibrium	In order to determine whether a product or reactant will be favoured at equilibrium, look at the relative stability of the charged species. The equilibrium will favour the side with the more stable charged species. If both species are charged, then look at the relative stability of the least stable species on each side.

Factors That Effect Molecule Stability:

1. **Resonance:** Allows delocalization of charge, leading to stabilization. The three resonance motifs are: $\pi - \sigma - \pi$; $\pi - \sigma-$ charge; $\pi - \sigma-$lone pair.
2. **Electronegativity:** Negative charge can be better stabilized by more electronegative species. Positive charge can be better stabilized by less electronegative (more electropositive) species. Comparison of electronegativity for stability is most important across a row on the periodic table. When comparing electronegativities of the same atom, electronegativity increases with increasing s-character of the orbital containing the charge.
3. **Polarizability:** More polarizable atoms can spread out charges better, and hence stabilize both negative and positive charges. Comparison of polarizability is most important down a column on the periodic table.
4. **Inductive Effects:** Nearby substituents can withdraw or donate electrons to help stabilize charge. This effect quickly drops off with increasing distance from the charge. More electronegative substituents are good electron withdrawing groups, helping to stabilize negative charge. Electron donating groups (alkyl groups, electron-rich groups) help stabilize positive charge.

Converting Between Equilibrium Constants and Percentages:

Let's say you know the equilibrium constant K for some reaction at equilibrium,

$$A \rightleftharpoons B$$

but would like to express the amount of each reagent in terms of its mole fraction (equal to percent divided by 100) of the total reaction mixture. This is NOT the same as K, but they are closely related. K is defined as

$$K = \frac{[B]}{[A]},$$

while the mole fraction of products and reactants is (respectively)

$$\chi_B = \frac{[B]}{[A]+[B]} \quad \text{and} \quad \chi_A = \frac{[A]}{[A]+[B]}.$$

We can easily write these numbers in terms of K using some simple algebra. Divide both the numerator and denominator of each fraction by $[A]$ or $[B]$ respectively to obtain

$$\chi_B = \frac{\frac{[B]}{[A]}}{\frac{[A]}{[A]} + \frac{[B]}{[A]}} = \frac{K}{1+K}$$

and

$$\chi_A = \frac{\frac{[A]}{[B]}}{\frac{[A]}{[B]} + \frac{[B]}{[B]}} = \frac{K^{-1}}{K^{-1}+1} = \frac{1}{1+K}.$$

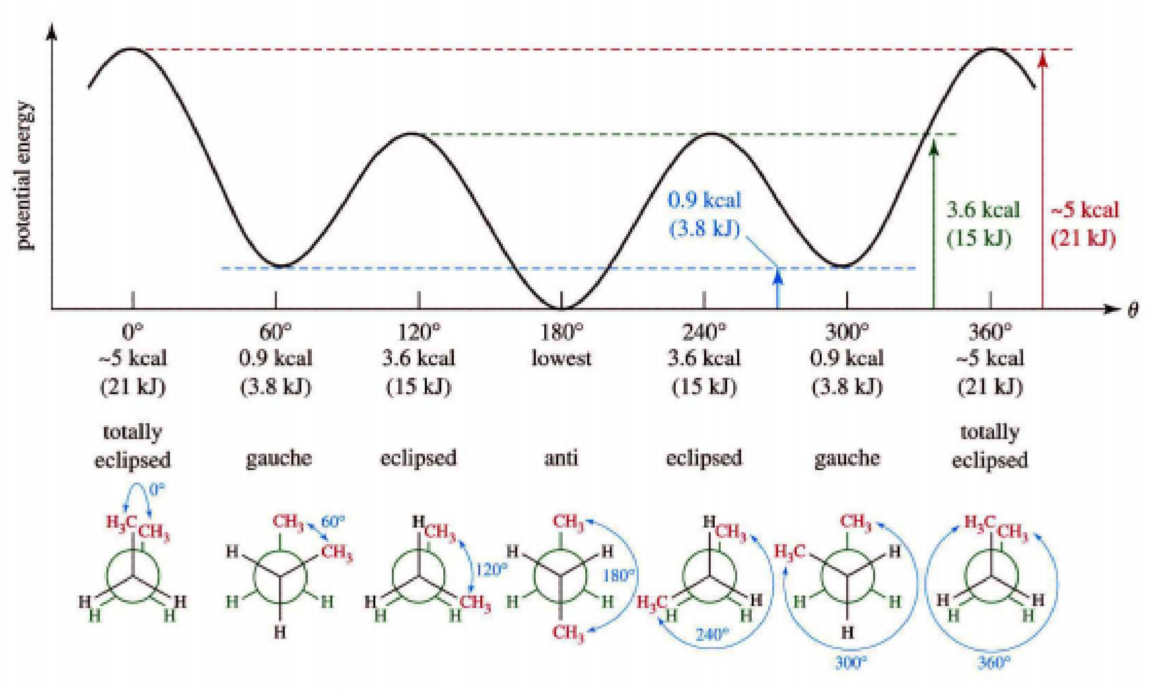


Figure 5: Plot of the energy of butane vs the dihedral angle.[4]

Equation/Concept	**Info About Equation/Concept**
Conformation	Different arrangements of atoms within a molecule that are a result of *rotating* about sigma bonds.
Butane Conformations	For the dihedral angle between terminal methyl groups: Syn = 0°; Gauche = 60°; Eclipsed = 120°; Anti = 180°. Notice in figure 5 eclipsed conformations are always higher energy than staggered conformations. Energy is further raised when bulky substituents are forced closer together.
Angle Strain	A property of closed ring structures in molecules that always raises energy. For example, if an sp^3 hybridized carbon is forced to take on a geometry with 90° bond angles as in cyclobutane, the energy of the system is raised because electrons in the bonding orbitals are forced closer together than they otherwise would be outside of a ring. Hence, cyclobutane is a relatively unstable compound. Six-membered rings have the lowest angle strain of any cyclic organic molecule, while smaller and slightly larger rings have higher angle strains. Very large ring structures do not have high angle strains.
Torsional Strain	Strain caused by the interaction between molecular orbitals in the bonds of a molecule. Torsional strain is the primary reason that some conformations of butane are more stable than others.
Steric Strain	Strain caused by the Coulombic repulsion between two bulky groups forced into close contact. Steric strain is the reason that the eclipsed syn conformation in butane is higher than other eclipsed conformations. In the syn conformation, two bulky methyl groups are forced close together in space. Steric strain is also the reason that large bulky molecules do not make good S_N2 nucleophiles, even it they are highly basic.
Cyclohexane Conformations	Two common conformations exist: chair or boat. Chair is always the lowest energy conformation. Chair flipping is possible, but must pass through a boat conformation. Chair flipping has the effect of changing all equatorial substituents to axial and vice versa. Therefore there are only two unique chair conformations, while there are up to six unique boat conformations. The lowest energy chair conformation is the one that most reduces 1,3-diaxial interactions. Other conformations are possible, but all are higher energy than the chair conformation and are therefore less relevant. The boat conformation can be thought of as a transition state between different chair conformations.

[4]Taken from: Wade, Jr., L.G. Organic Chemistry, 5th ed. Pearson Education Inc., 2003

Equation/Concept	**Info About Equation/Concept**
1,3-Diaxial Interactions	These are interactions of the three axial substituents in the chair conformation of cyclohexane on each of the two faces. 1,3-Diaxial interactions are reduced when as few bulky substituents as possible occupy axial positions. Longer bonded groups like Br do not have strong 1,3-diaxial interactions with short bonded groups.
CIP Priority Rules	(Cahn-Ingold-Prelog priority rules). Assign highest priority to the highest atomic number atom bonded to the stereocenter of interest. If there is a tie, consider atoms at distance 2 from the stereocenter. A list is made for each group of atoms bonded directly to the one directly attached to the stereocenter. Arrange each list in order of decreasing atomic number (and by atomic weight if different isotopes are present). Compare the lists atom-by-atom until the first point of difference is found. The group with the higher atomic number (or atomic weight) at this first point of difference is given the higher priority. If still tied, repeat the process for atoms at bond length 3, etc. If an atom A is double/triple-bonded to an atom B, A is treated as being singly bonded to two/three atoms: B and one/two "ghost atom(s)" that are duplicates of B but not attached to anything except atom A.
E/Z System	Used to name the absolute stereochemistry of geometric isomers (i.e. double bonded species). Rank priority of substituents on both sides of the double bond separately using the CIP rules. If the highest priority substituents are cis (same side): the double bond has the Z configuration. If the highest priority substituents are trans (opposite side): it has E configuration.
R/S System	Used for determining the absolute configuration of asymmetric centers. Rank the priority of substituents around an asymmetric center using the CIP rules. Point the lowest priority substituent backward and determine the direction from highest priority group to lowest ($1 \to 2 \to 3$). If clockwise, then the group has R configuration. If anticlockwise, the group has S configuration.
E/Z and R/S Nomenclature	Determine the underlying IUPAC root name as normal, then in brackets out in front of the name, list the positions of each stereocenter followed by its configuration in numerical order, separated by commas. (eg: (3S,5S)-5-bromo-3-chloro-5-fluoro-3-hexanamine).
Stereoisomers	Isomers of identical constitution (connectivity) but differing in the arrangement of their atoms in space. Can refer to enantiomers, diastereomers, or conformers.
Chirality	The property of a molecule or object of being non-superimposable with its own mirror image (e.g. hands are chiral). Chiral molecules cannot have a plane of symmetry or an inversion center. All chiral molecules rotate plane-polarized light in a particular direction (clockwise or anticlockwise).
Enantiomers	Two structures that that are non-superimposable mirror images of one another. Enantiomers must be chiral. Enantiomers have the (R/S) configuration at all asymmetric carbons flipped, but have the same (E/Z) configurations. Enantiomers have identical physical and chemical properties, except when interacting with other chiral compounds and in their interaction with plane-polarized light. Enantiomers rotate plane polarized light in opposite directions by the same amount.
Diastereomers	Two structures that have the same connectivity (are stereoisomers) but have at least one difference in the (R/S) configurations at asymmetric carbons, but not at all asymmetric carbons.
Meso Compounds	Compounds that would otherwise be chiral, but contain a plane of symmetry or inversion center which make them achiral. Meso compounds have asymmetric carbons arranged symmetrically, such that when the (R/S) configurations of all asymmetric carbons are flipped, an identical molecule is produced.
Racemic Mixture	A Racemic mixture is a mixture of enantiomers in equal proportion. Since both enantiomers are present, molecules within a racemic mixture will rotate plane polarized light in both directions in equal amounts. Therefore, a racemic mixture does not have a net effect on plane polarized light.
$[\alpha]_D^T = \frac{\alpha}{\ell[x]}$	The formula for the specific rotation of a chiral species, in degrees. α is a constant that depends on the particular chemical species and the temperature, ℓ is the path length, and $[x]$ is the concentration of the species.

Newman Projections

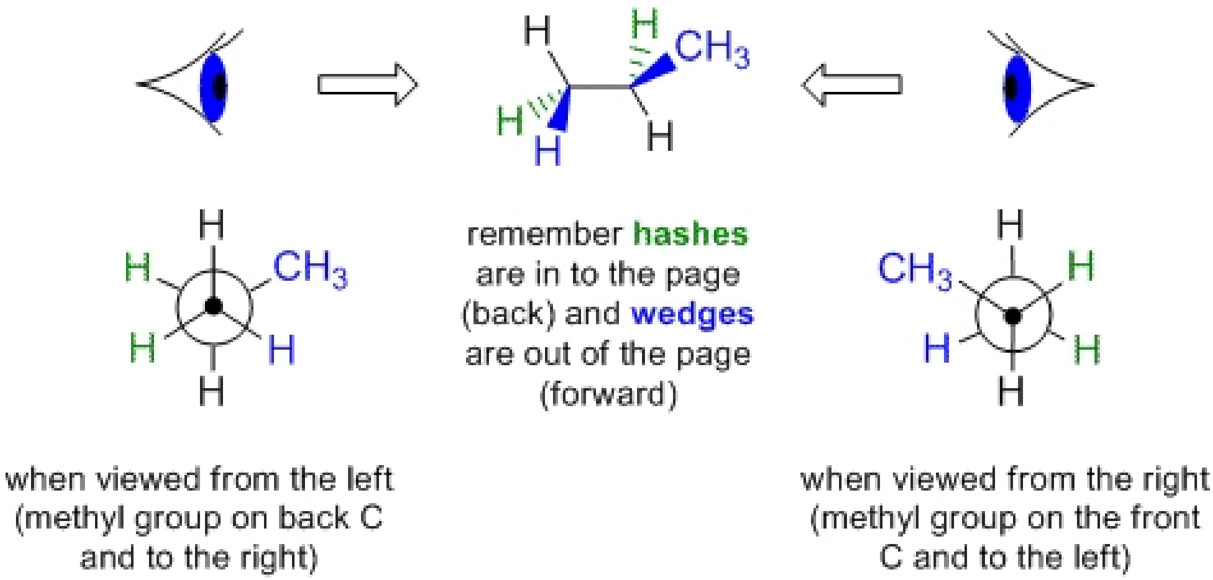


Figure 6: Newman projections are just another way of projecting 3D molecules onto a 2D page. [5]

Cyclohexane and Double Newman Projections

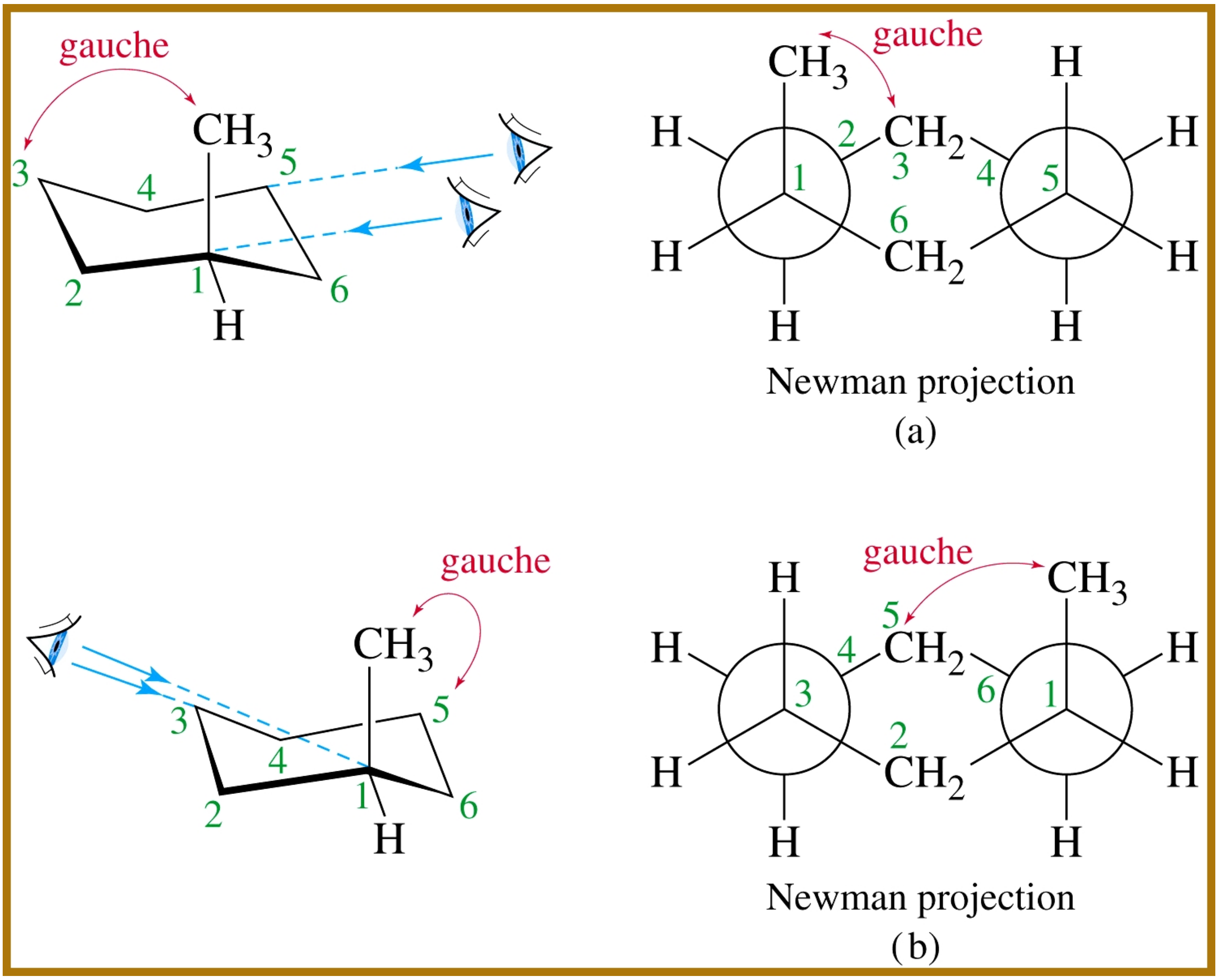


Figure 7: How to interpret double Newman projections for cyclohexane.[6]

[5]Taken From http://www.chem.ucalgary.ca/courses/350/Carey5th/Ch03/ch3-0-2.html
[6]Taken From http://wps.prenhall.com/wps/media/objects/340/348272/wade_ch03.html

Equation/Concept	Info About Equation/Concept
Chair Conformations	There are a maximum of only two possible chair conformations for any substituted cyclohexane, and they can be switched through a chair flip. Chair flipping requires energy as it must pass through the boat conformation (see figure 8). The boat conformation is always higher in energy than either of the chair conformations.
1,3-Diaxial Interactions	One of the two possible chair conformations of a substituted cyclohexane may be lower in energy, and therefore the preferred conformation. To determine which, look at the strength of the 1,3-diaxial interactions in each conformation.
Factors That Affect 1,3-Diaxial Interactions	• **Bond length.** Larger atoms like bromine or iodine have long bond lengths, and thus do not interact much through 1,3-diaxial interactions with hydrogen or methyl groups, but will interact with other groups that have long bonds! • **Degree of substitution.** When comparing the strength of 1,3-diaxial interactions for alkyl groups, look at the number of non-hydrogen groups bound to carbons that are in the axial orientation. Alkyl groups that are highly substituted *at the first carbon* interact more strongly through 1,3-diaxial interactions and are thus less stable. Substitution at carbons beyond the first carbon in a chain are less important, but still may play a small role in determining relative energies.

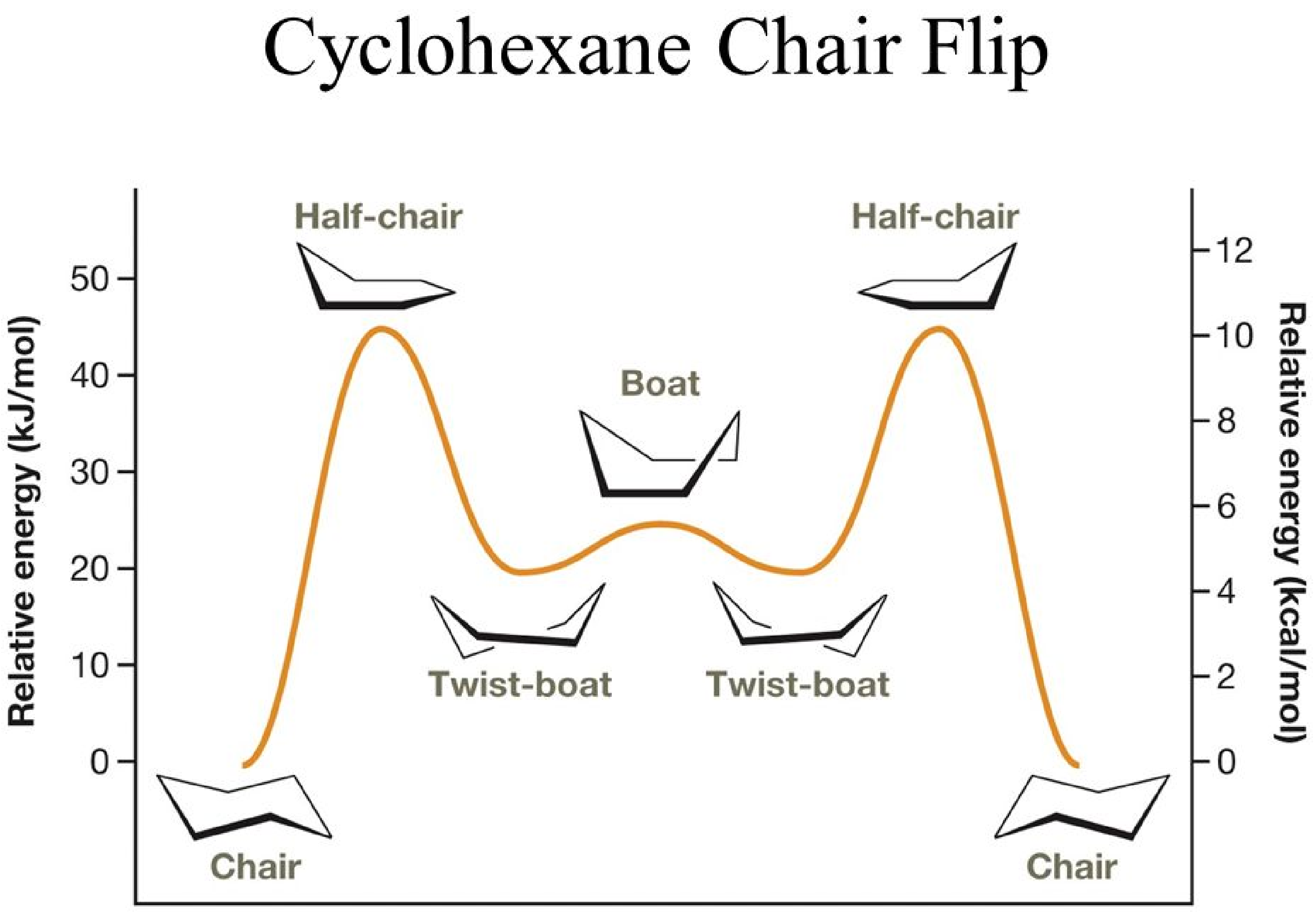


Figure 8: The relative stability of conformations for an unsubstituted cyclohexane. Notice that in order to move between chair conformations, an energy barrier must be overcome.[7]

[7]Taken from https://slideplayer.com/slide/9906415/

Fischer Projections

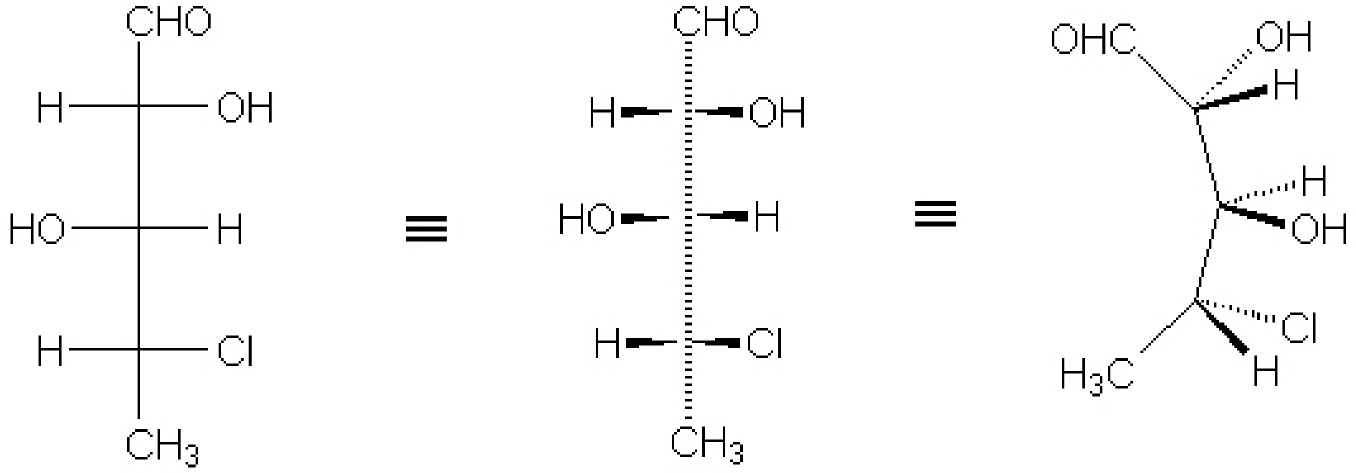


Figure 9: Fischer projections are a common way to draw linear carbohydrate molecules, but are not used much beyond that. They are useful for determining the stereochemistry of linear carbohydrate asymmetric centers.

Summary of S_N1 vs S_N2 Reactions

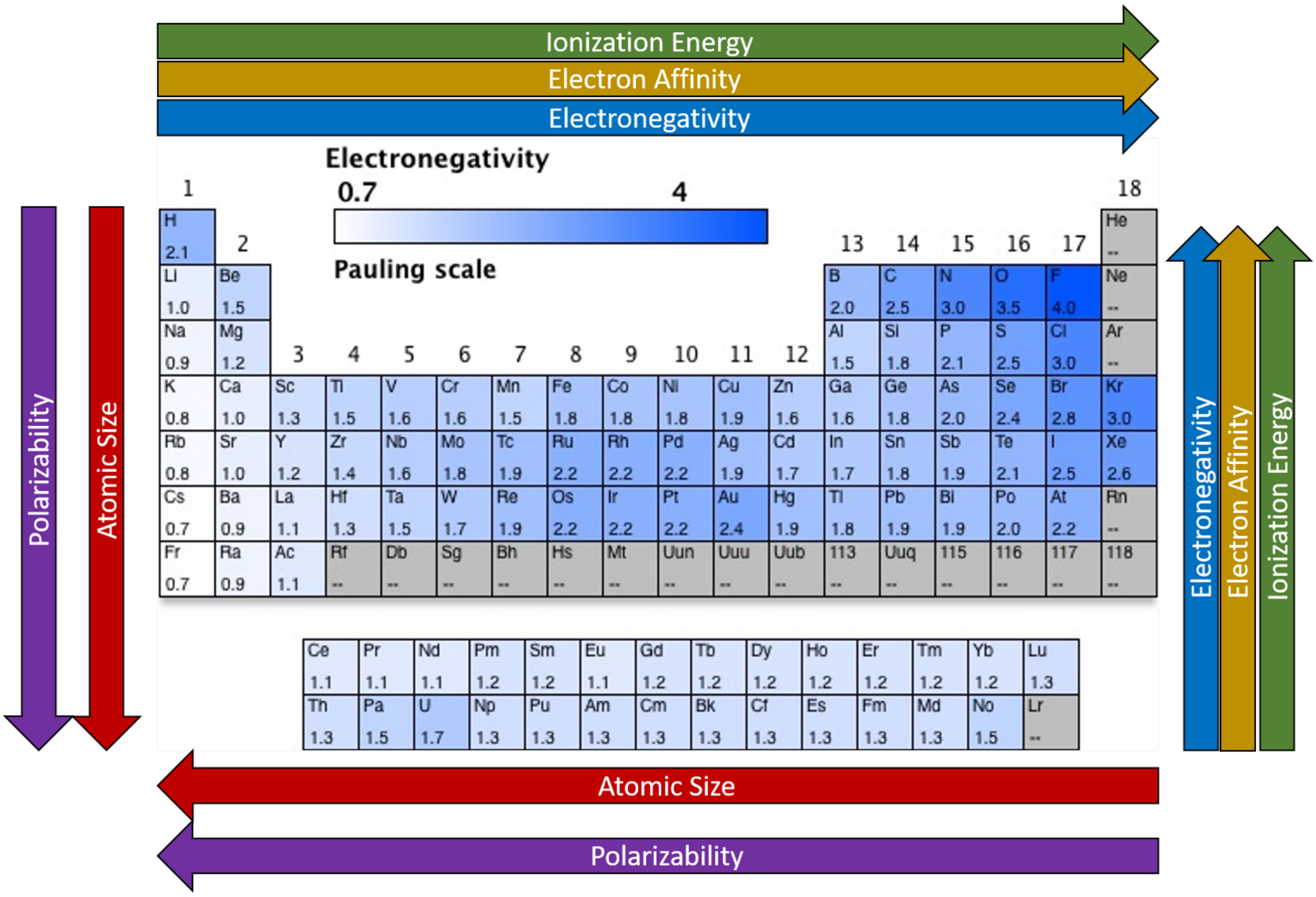
		SN2	SN1
characteristics	**mechanism**	simultaneous bond making and breaking	bond breaking first then bond making
	key intermed or TS	crowded TS	carbocation intermed
	stereochemistry	inversion of stereochem	both inversion and retention of stereochem
	rate	= k [R-X] [Nuc$^-$]	= k [R-X]
factors that effect the rate of reactions	R-X	**Methyl > 1° > 2°**	**3° > 2°**
	Nuc	**must be good Nuc$^-$**	can be weak (is often the solvent)
	LG	good LG is better	**must be good LG**
	solvent	more polar is better **(aprotic is better)**	more polar is better **(protic is better)**

- More substituted electrophiles form more stable carbocations due to electron donating inductive effects, and hence react more quickly through S_N1 reactions. More substituted electrophiles are less likely to react through S_N2 due to steric hindrance.
- In S_N1 reactions, the rate limiting step is the carbocation formation. Hence, the strength of the nucleophile is not very important.
- In S_N2 reactions, the rate limiting step is the formation of a concerted transition state. Stronger nucleophiles lower the energy of the transition state and hence improve reaction rates. Charged nucleophiles are generally better. More basic nucleophiles are better, unless they are bulky.
- Weak bases make good leaving groups for both types of substitution reaction. Weak bases are more stable as free species than strong bases, and hence do not raise the energy of the system too much upon dissociation.

- S_N1 can be catalyzed by protic solvents or acids in solution. A proton can be added to a bad leaving group, turning it into a better leaving group. Polar solvents also help to stabilize the carbocation intermediate.
- S_N2 reactions favor polar aprotic solvents, as these allow for stronger (charged) nucleophiles. Protic solvents will lose their proton to strong nucleophiles, making them weak. Polar protic solvents also tend to hydrogen bond with the nucleophile, creating a solvent shell around it and hindering its reactivity.
- Aprotic solvents do not solvate negatively charged nucleophiles that well. Therefore, negatively charged nucleophiles are more reactive in aprotic solvents.
- More polarizable nucleophiles react faster because they are not solvated as readily. Their charge is spread out more, so that van der Waals bonds to solvent molecules are weaker. Small nucleophiles are highly solvated, and tend to react slowly in S_N2 reactions. Relative polarizability for nucleophiles is most important along the same columns of the periodic table.
- Adjacent π-systems help stabilize electrophiles in both S_N1 and S_N2 reactions through the possibility of resonance. In S_N1 reactions the carbocation is stabilized by resonance, whereas in S_N2 the concerted transition state is stabilized by resonance.
- S_N2 reactions only occur on sp^3 hybridized carbons.
- The rate determining step of S_N2 reactions is a bi-molecular step. Hence it has second order kinetics and the rate of reaction depends on the concentrations of both the nucleophile and electrophile.
- The rate determining step of S_N1 reactions is unimolecular. Hence it has first order kinetics and the rate of reaction only depends on the concentration of the electrophile.

Physical Constants and Periodic Trends (for Reference)

Constant	Value and Units
Atomic mass unit (u)	$1\,\mathrm{u} = 1.660\,538\,9 \times 10^{-24}\,\mathrm{g}$ $1\,\mathrm{g} = 6.022\,142 \times 10^{23}\,\mathrm{u}$
Avogadro's number (N_A)	$N_A = 6.022\,142 \times 10^{23}\,\mathrm{mol^{-1}}$
Boltzmann's constant (k_B)	$k_B = 1.380\,648\,52 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ $k_B = R/N_A$
Gas constant (R)	$R = 8.314\,459\,8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ $= 8.314\,459\,8 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$ $= 8.314\,459\,8\,\mathrm{kg\,m^2\,s^{-2}\,K^{-1}\,mol^{-1}}$ $= 8.314\,459\,8\,\mathrm{m^3\,Pa\,K^{-1}\,mol^{-1}}$ $= 0.082\,057\,338\,\mathrm{L\,atm\,K^{-1}\,mol^{-1}}$ $= 1.987\,203\,6 \times 10^{-3}\,\mathrm{kcal\,K^{-1}\,mol^{-1}}$ $= 8.205\,733\,8 \times 10^{-5}\,\mathrm{m^3\,atm\,K^{-1}\,mol^{-1}}$ $= k_B N_A$
Mass of electron (m_e)	$m_e = 5.485\,799 \times 10^{-4}\,\mathrm{u}$ $= 9.109\,383 \times 10^{-28}\,\mathrm{g}$
Mass of proton (m_p)	$m_p = 1.007\,276\,5\,\mathrm{u}$ $= 1.672\,621\,7 \times 10^{-24}\,\mathrm{g}$
Mass of neutron (m_n)	$m_n = 1.008\,664\,9\,\mathrm{u}$ $= 1.674\,927\,3 \times 10^{-24}\,\mathrm{g}$
Planck constant (h)	$h = 6.626\,069 \times 10^{-34}\,\mathrm{J\,s}$
Reduced Planck constant ($\hbar$)	$\hbar = h/2\pi = 1.054\,572\,66 \times 10^{-34}\,\mathrm{J\,s}$
Speed of light (c)	$c = 2.997\,924\,58 \times 10^{8}\,\mathrm{m\,s^{-1}}$



Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.01																	2 He Helium 4.00
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.88	23 V Vanadium 50.94	24 Cr Chromium 51.99	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 84.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium 98.91	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.6	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.85	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.20	83 Bi Bismuth 208.98	84 Po Polonium [208.98]	85 At Astatine 209.98	86 Rn Radon 222.02
87 Fr Francium 223.02	88 Ra Radium 226.03	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium 144.91	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.06	71 Lu Lutetium 174.97
89 Ac Actinium 227.03	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.05	94 Pu Plutonium 244.06	95 Am Americium 243.06	96 Cm Curium 247.07	97 Bk Berkelium 247.07	98 Cf Californium 251.08	99 Es Einsteinium [254]	100 Fm Fermium 257.10	101 Md Mendelevium 258.10	102 No Nobelium 259.10	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Metalloid | Nonmetal | Halogen | Noble Gas | Lanthanide | Actinide