

# CHEM 205: Summary of Important Concepts

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## Thermodynamics

Equation/Concept	Info About Equation/Concept
System	The system is defined as a group of material and/or radiative contents that we wish to focus our attention on. Its 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 <b>do not depend on the path taken</b> to get to a given thermodynamic state. Examples: temperature, pressure, internal energy, enthalpy, 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.

Equation/Concept	Info About Equation/Concept
Kinetic Molecular Theory for Ideal Gases	<p>The kinetic molecular theory for ideal gases makes four basic assumptions about the nature of gas particles:</p> <ol style="list-style-type: none"> <li>1. Ideal gases are comprised of a large number of <b>point particles</b>.</li> <li>2. Gas particles do not interact with each other through long-range attractive or repulsive forces.</li> <li>3. All collisions involving gas particles are <b>elastic</b> (kinetic energy is conserved).</li> <li>4. An ideal gas is isotropic: it behaves the same in all spatial directions.</li> </ol> <p>From these basic assumptions, the <b>ideal gas law</b> follows.</p>
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, translational 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.
$E_{trans} = \frac{3}{2}RT$	For ideal gases, $E_{trans} = E$ since they have no other forms of energy storage. $\epsilon_{trans} = \frac{3}{2}k_B T$ is the single-molecule equivalent. Hence, the internal energy of an ideal gas is a function only of temperature: $E = E(T)$ . For real gases, $E = E(T, V)$ .
Principle of Equipartition	A result (derivable from classical statistical mechanics) which states that each <b>degree of freedom</b> $f$ contributes $\frac{1}{2}RT$ to the total molar internal energy. In this context a degree of freedom is defined as any possible form of energy storage such as translation, rotation, vibration, or electronic excitation. Ideal gases only have 3 degrees of freedom, corresponding to translation in the $x$ , $y$ , and $z$ directions. Hence their total internal energy is as above.
$E = \frac{5}{2}nRT$	The total internal energy of a <b>diatomic molecule at ambient temperatures</b> . A diatomic molecule has 3 translational degrees of freedom, plus two rotational degrees of freedom, corresponding to its two primary axes of rotation. The third axis of rotation (along the bond axis) corresponds to a rotation with infinite energy level spacing (if one assumes the nuclei are point masses). Hence this rotational degree of freedom is “frozen out”: rotations along the bond axis do not allow for energy storage. Vibrational and electronic degrees of freedom are also “frozen out” at ambient temperatures (around 300 K) due to their relatively large energy level spacings, and hence do not contribute to the total internal energy.
$Z = \frac{PV}{nRT}$	$Z$ is called the <b>compressibility factor</b> , and is identically equal to 1 for ideal gases. Real gases show deviations from $Z$ . If intermolecular forces are dominated by attractive interactions, then $Z < 1$ and the pressure will be <b>less than ideal</b> . If intermolecular forces are dominated by repulsive interactions, then $Z > 1$ and the pressure will be <b>greater than ideal</b> . Real gases may show both behaviors over a range of temperatures and pressures.
$T_B$	<b>The Boyle Temperature:</b> a specific system-dependent temperature for real gases where the bulk effects of 2-body attractive and repulsive interactions exactly balance out. At the Boyle temperature, the second virial coefficient becomes negligible and gases behave ideally over a large range of pressures. Once densities become large enough to allow for a significant contribution from the third virial expansion term, such gases will tend towards $Z > 1$ .
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 <i>by the system</i> , negative $w$ ) or a contraction (work done <i>on the system</i> , positive $w$ ) of the system. Work only exists during a change in the system, it is a path variable.
Zeroth Law of Thermodynamics	<i>Two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another.</i> 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.

Equation/Concept	Info About Equation/Concept
$\Delta E = q + w$	This is the equation for the <b>first law of thermodynamics</b> . It states that the change in energy <i>of the system</i> is equal to the heat flow $q$ into the system (positive $q$ is heat flow <i>into</i> the system) plus the work done on the system $w$ . Work done <i>on the system</i> corresponds to positive $w$ . This is simply a statement of the conservation of energy and only applies <i>for a particular path</i> .
$\text{d}w = -P_{\text{ext}}\text{d}V$	The most general definition of the increment of work. This equation is for the <i>improper</i> increment of work done <i>on</i> the system. It is improper because work is a path variable, so the increment of work done is not an exact differential. This equation <b>always applies</b> .
$w = - \int_{V_i}^{V_f} P_{\text{ext}}\text{d}V$	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 $\text{d}w$ from the initial state to the final state. This is the most general expression for work done and it <b>will always apply</b> .
$w = -nRT \ln\left(\frac{V_f}{V_i}\right)$	This is the work done on an <b>ideal gas</b> expanding/contracting <b>reversibly and isothermally</b> . In this situation, $P_{\text{ext}} = P_{\text{sys}} = \frac{nRT}{V}$ 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 <b>constant external pressure</b> . This follows directly from the definition of total work done for the case in which $P_{\text{ext}}$ is a constant.
$w = 0$	The total work done for a process is zero only when either: (1) the <b>external pressure is zero (free expansion)</b> or (2) the <b>system volume is held fixed</b> (such that $\text{d}V = 0$ ).
$w = w_{\text{max}}$	Work done <b>by a system on the surroundings</b> is maximized during a <b>reversible expansion</b> .
$w = w_{\text{min}}$	Work done <b>on the systems by the surroundings</b> is minimized during a <b>reversible compression</b> . This amount of work will be exactly equal to the previous case of reversible expansion, hence the term <i>reversible</i> .
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 $U = C_{V,m}nT$ , where $C_{V,m}$ is the constant-volume molar heat capacity ( $\frac{3}{2}R$ for an ideal 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 fixed.
$PV = nRT$	This is the ideal gas law. It is the <i>equation of state</i> 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 $T$ .
$P_1V_1 = P_2V_2$	This equation is true only for an ideal gas undergoing an isothermal or constant $T$ process. It is true whether the process is reversible or not, since $PV$ is proportional to the internal energy $E$ , and an ideal gas process at constant $T$ will have an unchanged $E$ .
$P = \sum_i P_i = \sum_i \frac{n_iRT}{V}$	The equation of state for a mixture of ideal gases. $P_i$ is called the <b>partial pressure</b> 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 <b>mole fraction</b> $x_i$ .
Isothermal Process	An isothermal process is a process that maintains the system at a constant temperature along <b>the entire path</b> from its initial state to its final state.

Equation/Concept	Info About Equation/Concept
Constant $T$ Process	A process which maintains the initial and final states of the system at 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. <b>Adiabatic walls</b> are system boundaries that do not allow exchange of heat. They are the walls of an isolated system. Inversely, <b>Diathermal walls</b> 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.
Isobaric Process	An isobaric process is a process that occurs with no change in system pressure along the entire path from initial to final state.
Isochoric Process	An isochoric process is a process that occurs with no change in system volume along the entire path from initial to final state.
$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$	<p>The <b>van der Waals equation of state</b>. This equation of state, when properly parameterized with <math>a</math> and <math>b</math>, provides a more reasonable approximation to the relationship between state variables of real gases than does the ideal gas law. The <math>a</math> parameter of the van der Waals equation of state attempts to capture the bulk effects of <b>attractive intermolecular interactions</b>. The attractive interaction correction term is also proportional to the square of the density (<math>\frac{n}{V}</math>) based on the following arguments: only molecules near the edge of a container will, on average, have a net attractive force inward since molecules in the bulk will have attractive forces from all directions that cancel out. The number of molecules near the edge of the container is proportional to the density, and the strength of the attractive interactions on a molecule at the edge of the container is also proportional to the density. Combining these two arguments results in a correction which is overall proportional to the density squared.</p> <p>The <math>b</math> parameter represents the excluded volume created by the <b>size</b> of a gas molecule, i.e. the excluded volume due to perfectly hard core (assumption). The total excluded volume is then simply this molecular volume times the number of molecules. Both <math>a</math> and <math>b</math> are different for each species of gas, and can only be determined from experiment.</p>
$P(T, \rho) = RT \left[ \rho + \sum_{i=2}^{\infty} B_i(T) \rho^i \right]$	<p>This equation is known as the <b>Virial Equation of State</b>, or simply the <b>Virial Expansion</b>. It is the result of thermodynamic perturbation theory applied to the ideal gas law. The idea is to expand equation of state of a real gas in terms proportional to powers of density <math>\rho = \frac{n}{V}</math>. Higher order terms in the expansion are generally less important, but this assumption breaks down at very high pressure, when the gas transitions to a liquid or solid. The temperature-dependent coefficients <math>B(T)</math> are called virial coefficients, which make corrections to the ideal gas equation due to <math>i</math>-body interactions (e.g. the second virial coefficient accounts for 2-body interactions). Virial coefficients depend on temperature since the effect of intermolecular interactions depends on a molecule’s kinetic energy. Molecules moving slowly may tend to clump together due to attractive interactions, whereas fast moving molecules will mainly experience the effects of short-range repulsive interactions.</p>
$df(x_1, \dots, x_N) = \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}} dx_i$	<p>The general definition of the <b>total differential</b> for a function of <math>N</math> variables. This exact mathematical expression is frequently used in thermodynamics to obtain a differential form of some state function <math>f</math> in terms of other state variables <math>\{x_i\}</math>. Note that the partial derivatives are calculated with all other variables held fixed.</p>

Equation/Concept	Info About Equation/Concept
$H = E + PV$	Definition of <b>enthalpy</b> . 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 <b>exothermic</b> and when a process results in $\Delta H > 0$ it is called <b>endothermic</b> . Reaction enthalpy alone is not enough to determine whether or not the process will proceed spontaneously.
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 <b>extensive</b> 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.
$dq = CdT = mC_{sp}dT = nC_mdT$	The incremental heat flow into the system is the product of the heat capacity $C$ (at that temperature) and the incremental change in temperature $dT$ . Note that $C$ is an extensive variable. If $C$ is independent of $T$ over the range of interest, then we can integrate to yield $q = C\Delta T = mC_{sp}\Delta T = nC_m\Delta T$ .
$\Delta E = \int_{T_1}^{T_2} nC_{V,m}dT = q_V$	For a constant volume process, the change in internal energy can be measured as the integral of the <b>constant-volume heat capacity</b> $C_{V,m}$ . Since no work can be done for a constant volume process, the first law tells us that this is also the heat flow into the system.
$\Delta H = \int_{T_1}^{T_2} nC_{P,m}dT = q_P$	For a constant pressure process, the change in internal enthalpy is simply the integral of the <b>constant-pressure heat capacity</b> $C_{P,m}$ . This is also equal to the heat flow into the system at constant pressure.
$C_P = C_V + nR$	Only true exactly for an <b>ideal gas</b> , this equation tells us that the constant pressure heat capacity is greater than the constant volume heat capacity. The physical reason for this is that the constant volume heat capacity does not allow for any added energy to be used for work. All heat absorbed is used to increase the temperature. Under constant pressure conditions, some heat absorbed is used to expand the system, requiring work to be done. This partitions some of the absorbed energy into work done, which does not increase the temperature of the system.
$C_{V,m} = \frac{3}{2}R$	The exact constant volume molar heat capacity for an <b>ideal gas</b> . This can be derived from the equipartition theorem, since ideal gases only have three translational degrees of freedom. This is also the approximate heat capacity for a monatomic real gas at ambient temperatures, and the <b>translational contribution</b> to the constant-volume heat capacity for any real gas.
$C_{P,m} = \frac{5}{2}R$	The exact constant pressure molar heat capacity for an <b>ideal gas</b> . This will also be the approximate heat capacity for a monatomic real gas at ambient temperatures.
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 <i>ambient</i> temperature is defined as $T = 298.15 \text{ K}$ .

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$\Delta H_f^\circ$	$\Delta H_f^\circ$ is the <b>standard enthalpy of formation</b> , sometimes called the <b>standard heat of formation</b> . It is defined as the change in enthalpy required to create <b>one mole</b> 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, $0 \text{ kJ mol}^{-1}$ . Because $\Delta H_f^\circ$ depends on temperature, the temperature at which the standard enthalpy of formation applies must be defined. However, $T$ is often assumed to be 298.15 K.
$\Delta H_{\text{rxn}}^\circ = \sum_{\text{P}} \Delta H_{\text{f,P}}^\circ - \sum_{\text{R}} \Delta H_{\text{f,R}}^\circ$	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.
$\Delta H \approx \Delta E + RT(\Delta n_{\text{gas}})$	This equation only applies at <b>constant temperature</b> makes two assumptions: (1) The change in volume of a reaction is caused primarily by the change in the number of moles of gas; the volume of liquids and solids is negligible. (2) Gases can be treated with the ideal gas equation.
Entropy $S$	Entropy is an extensive state variable that can be thought of as <b>a measure of the dispersal of energy</b> within a system. Many people think of entropy as a measure of system <b>disorder</b> , 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.
$S_f^\circ$	The <b>standard entropy of formation</b> . Defined similarly to the standard enthalpy of formation, only that the zero of entropy is defined by the third law of thermodynamics, so that it is an absolute value.
$\Delta G_f^\circ$	The standard Gibbs free energy of formation. Defined in the same way as the standard enthalpy of formation.
$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_P dT$	<b>Kirchoff's Equation</b> . Useful when trying to calculate the enthalpy of a reaction at constant pressure when the enthalpy is already known at some temperature $T_1$ , but you would like to know the enthalpy change at $T_2$ . This equation can also be applied to entropies, but the integral takes on an extra multiplicative factor of $\frac{1}{T}$ .
$\Delta S_{\text{Universe}} \geq 0$	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 $\Delta S_{\text{Universe}}$ is the change in entropy of the <i>entire universe</i> 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.
$dS = \frac{\text{d}q_{\text{rev}}}{T}$	The defining equation for <b>entropy</b> . It is calculable only along a reversible path, but once calculated the resulting $\Delta S$ applies to any path between the initial and final state (entropy is a state function). This definition implies a well defined temperature $T$ which requires the system to be in thermal and mechanical equilibrium (i.e. follows a reversible path). Note that we cannot calculate $\Delta S$ from the actual heat change of a real (irreversible) process.

Equation/Concept	Info About Equation/Concept
$dS \geq \frac{\delta q}{T_{\text{Surr}}}$	The Clausius inequality. This is another expression of the second law of thermodynamics, and is only <b>equal for a reversible process</b> . The inequality applies for irreversible processes where 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.
$\Delta S_{IS} \geq 0$	Another expression of the <b>Second Law of Thermodynamics</b> , where IS stands for <b>Isolated System</b> . For any isolated system not at equilibrium, entropy will always increase over time until equilibrium is established. Once an isolated system reaches equilibrium, entropy remains fixed.
$\Delta S = \frac{\Delta H}{T}$	This equation applies for a <b>constant P and constant T reversible process only</b> . For example, a phase change at constant T and P in which $\Delta H$ would be the enthalpy change for the phase transition.
$dE = TdS - PdV$	This is one of the <b>Fundamental Equations of Thermodynamics</b> , since it incorporates both the first and second laws of thermodynamics. This expression assumes a reversible processes, hence it is not strictly true for irreversible processes but may still be used if one can produce a hypothetical reversible pathway between two states.
$dE = TdS$	Applicable under <b>constant volume</b> conditions. Allows for an easy way to measure entropy changes under such conditions.
$dS = \frac{dE}{T} = \frac{nC_{V,m}dT}{T}$	This equation is applicable under <b>constant volume</b> conditions, allowing a measurement of entropy change by way of heat capacity.
$\Delta S = \int_{T_1}^{T_2} \frac{nC_{V,m}dT}{T}$	The integral version of the above equation, allowing for measurement of finite changes in entropy if one can measure the constant volume heat capacity as a function of T. This equation requires <b>constant V conditions</b> .
$\Delta S = nC_{V,m} \ln \left( \frac{T_2}{T_1} \right)$	Applicable to <b>constant volume</b> measurements only when $C_{V,m}$ is not a function of temperature. This is often useful for small changes in temperature or for ideal gases.
$dH = TdS + VdP$	Another <b>Fundamental Equation of Thermodynamics</b> pertaining to incremental changes in enthalpy. This expression applies to <b>reversible processes</b> .
$dH = TdS$	This equation is applicable under <b>constant pressure</b> conditions. Shows the simple connection between entropy and energy under such conditions.
$dS = \frac{dH}{T} = \frac{nC_{P,m}dT}{T}$	This equation is applicable under <b>constant pressure</b> conditions, allowing a measurement of entropy changes by way of heat capacity.
$\Delta S = \int_{T_1}^{T_2} \frac{nC_{P,m}dT}{T}$	The integral version of the above equation, allowing for measurement of finite changes in entropy if one can measure the constant pressure heat capacity as a function of T. This equation requires <b>constant P conditions</b> .
$\Delta S = nC_{P,m} \ln \left( \frac{T_2}{T_1} \right)$	Applicable to <b>constant pressure</b> measurements only when $C_{P,m}$ is not a function of temperature. This is often useful for small changes in temperature or ideal gases.
$dS = \frac{nC_{V,m}}{T}dT + \frac{P}{T}dV$	Applicable for a reversible process when only PV work is done.

Equation/Concept	Info About Equation/Concept
$\Delta S = \frac{3}{2}nR \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)$	Applicable for a reversible process when only $PV$ work is done, involving an ideal gas. Derived by integrating the above equation assuming the ideal gas law applies and the heat capacity is independent of $T$ . This equation essentially comes from deriving a reversible pathway with two parts: variation of $T$ with $V$ fixed, then variation of $V$ with $T$ fixed.
$dS = \frac{nC_{P,m}}{T}dT - \frac{V}{T}dP$	Applicable for a reversible process when only $PV$ work is done. Note that this is exactly equivalent to the equation two above.
$\Delta S = \frac{5}{2}nR \ln \left( \frac{T_2}{T_1} \right) - nR \ln \left( \frac{P_2}{P_1} \right)$	Applicable for a reversible process when only $PV$ work is done, involving an ideal gas. Derived by integrating the above equation assuming the ideal gas law applies and the heat capacity is independent of $T$ . This equation essentially comes from deriving a reversible pathway with two parts: variation of $T$ with $P$ fixed, then variation of $P$ with $T$ fixed.
$(dq_{irrev})_{Sys} = -(dq_{rev})_{Surr}$	Since the surroundings constitute everything in the universe that is not contained in the system and are effectively infinite, we can treat the surroundings as able to act as a perfect isothermal heat sink or source, capable of absorbing or releasing the actual heat from or to the system in a reversible manner. Additionally, all heat that flows into or out of the system must come from the surroundings.
$A = E - TS$	The definition of <b>Helmholtz Free Energy</b> , a quantity which is most useful under <b>constant <math>T</math> and <math>V</math> conditions</b> . Under such conditions, the Helmholtz free energy acts as a thermodynamic potential which is minimized at equilibrium. Any spontaneous changes under constant $T$ and $V$ must proceed with a reduction in $A$ .
$dA = dE - TdS$	The differential version of the Helmholtz free energy under <b>constant temperature conditions</b> .
$(dA)_{T,V} \leq 0$	Condition for spontaneity (inequality) and equilibrium (equality) under constant $T$ and $V$ conditions.
$dA = -SdT - PdV$	Another <b>fundamental equation of thermodynamics</b> , this one is expressed for the Helmholtz free energy. This expression applies to reversible processes.
$G = H - TS$	Definition of <b>Gibbs free energy</b> . Gibbs free energy is the criterion for determining if a process will proceed when the system is at constant $P$ and $T$ . Reactions in which $\Delta G < 0$ are said to be <b>exergonic</b> . 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 <b>endergonic</b> , and are not spontaneous at constant $T$ and $P$ .
$dG = dH - TdS$	The differential version of Gibbs free energy under <b>constant temperature conditions</b> .
$(dG)_{T,P} \leq 0$	The criterion for spontaneity (inequality) or equilibrium (equality) when a system is under constant $T$ and $P$ conditions.
$dG = VdP - SdT$	Another <b>fundamental equation of thermodynamics</b> , this one expressed for the Gibbs free energy. This expression applies to reversible processes.
$\Delta G_{\text{System}} = -T\Delta S_{\text{Universe}}$	At <b>constant temperature and pressure</b> , 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 $\Delta G$ corresponds to a process that <i>may</i> proceed spontaneously, as long as the activation barrier is much greater than $k_B T$ .



Equation/Concept	Info About Equation/Concept
$\Delta G^\circ = -RT \ln(K)$ $= \Delta H^\circ - T\Delta S^\circ$ $K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$	The standard Gibbs free energy. $\Delta G^\circ$ 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 mol L <sup>-1</sup> 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 statistical mechanical definition of entropy for an isolated system. $\Omega$ is the number of <b>accessible quantum states</b> to a system 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 $\Delta H$ 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.
$S^\circ$	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.
$S_{0\text{ K, perfect crystal}} = 0$	The <b>Third Law of Thermodynamics</b> . Here $S_{0\text{ K, perfect crystal}}$ refers to the entropy of a pure, perfectly crystalline solid at 0 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 $S = k_B \ln(1) = 0$ . The third law of thermodynamics also states that it is impossible to reduce the temperature of any system to absolute zero in any finite number of cooling cycles.

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

Sign of $\Delta H$	Sign of $\Delta S$	Sign of $\Delta G$	Spontaneous?
+	+	+ (Low $T$ ) OR - (High $T$ )	At High $T$
+	-	+	Never
-	+	-	Always
-	-	+ (High $T$ ) OR - (Low $T$ )	At Low $T$

## Thermodynamics of Acids and Bases (Review)

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 <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , HClO <sub>4</sub> . Strong bases to know: NaOH, KOH, Ca(OH) <sub>2</sub> . 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 °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 <b>conjugate pair</b> 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 °C. The water self-dissociation constants in terms of negative logs.
$[AH]_{\text{Buffer}} \approx 0.1[A^-] \text{ to } 10[A^-]$	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 <i>buffer solution</i> . 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.
$\beta = \frac{\Delta n}{\Delta pH}$	$\beta$ 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, $\Delta n$ is the number of equivalents of strong acid/base added per liter of solution, and $\Delta pH$ is the resulting change in pH. The buffer capacity is maximized when the ratio of conjugate acid to conjugate base is 1:1.

## Thermodynamics of Phases and Solutions

Equation/Concept	Info About Equation/Concept
Phase Diagram	A phase diagram is a 2D plot of any two thermodynamic variables (usually $P$ and $T$ ) which displays the thermodynamically stable phase (solid, liquid, gas), i.e. lowest Gibbs free energy phase, of a system as a function of its thermodynamic state.

Equation/Concept	Info About Equation/Concept
$\left(\frac{\partial G}{\partial P}\right)_T = V$	Derived from the fundamental thermodynamic equation for the Gibbs free energy assuming only one pure chemical species. This relationship is useful to when interpreting $T$ vs $P$ phase diagrams. If one fixes $T$ and plots $G$ vs $P$ , then the resulting slope will always be positive and equal to $V$ . The slope will be much greater for gases than condensed phases.
$\left(\frac{\partial G}{\partial T}\right)_P = -S$	Derived from the fundamental thermodynamic equation for the Gibbs free energy assuming only one pure chemical species. This relationship is useful to when interpreting $T$ vs $P$ phase diagrams. If one fixes $P$ and plot $G$ vs $T$ , the slope will be $-S$ . Since $S \geq 0$ , the slope will always be negative. The steepness of the slope will follow the series $S_g \gg S_l > S_s$ .
$\left(\frac{dP}{dT}\right)_{PB} = \frac{\Delta S}{\Delta V} = \frac{-\left(\frac{\partial \Delta G}{\partial T}\right)_P}{\left(\frac{\partial \Delta G}{\partial P}\right)_T}$	The <b>Clapeyron Equation</b> . $PB$ stands for <b>Phase Boundary</b> , which is where this equation applies. This equation states that, when viewing a $P$ - $T$ phase diagram along a phase boundary, the slope of the phase boundary is equal to the change in entropy divided by the change in volume for a system proceeding along this line. For a solid-liquid phase boundary, we expect that $\Delta V$ will be tiny and usually positive (most liquids occupy more volume than solids), so the slope of a solid-liquid phase is typically steep and positive, with the notable exception of water which is steep and negative. For a liquid-gas or solid-gas transition, $\Delta V$ will be very large and always positive (gases always occupy more volume than solids), so the resulting slope of such a phase boundary on a $P$ vs $T$ diagram is small and positive. Note that this equation is exact, no assumptions are made in its derivation.
$\left(\frac{dP}{dT}\right)_{PB} = \frac{\Delta H_{vap}}{T\Delta V}$	Another form of the <b>Clapeyron Equation</b> , which is also exact at each $T$ and $P$ along a phase boundary.
Triple Point	A triple point is the single thermodynamic state (i.e. pair of $P$ and $T$ for a pure system) where three phases (often solid, liquid, and gas) can coexist in equilibrium. Triple points can also exist when two or more different solid phases exist for a system, in which case a triple point may exist between any two intersecting phase boundaries. For example, water has several high-pressure solid phases resulting in at least 9 triple points which occur at pressures above 1900 atm.
$F = C - p + 2$	The <b>Gibbs Phase Rule</b> . This relationship defines the number of thermodynamic degrees of freedom $F$ , i.e. how many thermodynamic variables are free to vary independently for a given thermodynamic state. $C$ is the number of independent chemical components required to define the system and $p$ is the number of phases present. For pure, one component systems, $C = 1$ and the equation becomes $F = 3 - P$ . For example, a pure system with a single phase ( $p = 1$ ) has two thermodynamic degrees of freedom: both $T$ and $P$ can be varied freely without changing the phase of the system. When two phases are present, corresponding to a phase boundary on a phase diagram, any given $T$ has only one $P$ which will keep the system on that phase boundary. Hence there is only one thermodynamic degree of freedom along a phase boundary. For three phases to be present, both $T$ and $P$ can only be one value: that of the triple point. No thermodynamic degrees of freedom exist for such a system.
$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$	The integrated form of the <b>Clausius–Clapeyron equation</b> . This equation is derived from the Clapeyron equation by making three assumptions: (1) that $\Delta H_{vap}$ is independent of both $T$ and $P$ ; (2) that the volume of the gas is much greater than the volume of the liquid, such that $\Delta V = V_g - V_l \approx V_g$ ; and (3) That the vapour phase can be treated as an ideal gas. Plots of $\ln(P)$ vs $\frac{1}{T}$ where $P$ is the vapour pressure will have a slope of $-\frac{\Delta H_{vap}}{R}$ . This equation can be equally well applied to solid systems that sublime, where $\Delta H_{vap}$ must be replaced by $\Delta H_{sub}$ .
$\frac{dP}{P} = \frac{-\Delta H_{vap}}{RT^2} dT$	The differential form of the Clausius–Clapeyron equation.

Equation/Concept	Info About Equation/Concept
$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_B} \approx 10.5R$	A simple empirical relationship known as <b>Trouton's Rule</b> , which gives a decent approximation to entropy and enthalpy of vaporization for systems dominated by <b>van der Waals forces</b> . Does not work well for systems like water, dominated by hydrogen bonding because the hydrogen bonding in the liquid phase lowers the entropy of the liquid, raising the difference in entropy between liquid and gas.
$\Delta G_T = \int_{P_1}^{P_2} V dP = nRT \ln \left( \frac{P_2}{P_1} \right)$	The first equality is true in general for an <b>constant temperature process</b> , whereas the second is only true for an <b>ideal gas</b> undergoing a constant $T$ process. Notice that the change in Gibbs free energy of an ideal gas at constant $T$ is not zero. This is entirely entropy driven.
$G_P - G^\circ = nRT \ln \left( \frac{P}{P^\circ} \right)$	For an <b>ideal gas</b> at constant pressure, we can find the Gibbs free energy change relative to a <b>standard state</b> (denoted with $\circ$ ) by comparing the pressure to the <b>standard state pressure</b> . The standard pressure $P^\circ \equiv 1 \text{ atm}$ .
$G_P - G^\circ = nRT \ln(a)$	In order to maintain the same functional form for the Gibbs free energy relative to a standard state, we define the unitless quantity <b>activity</b> $a$ which accounts for any non-ideal behaviour in a system. For an ideal gas, $a = \frac{P}{P^\circ}$ .
$a = \frac{\phi P}{P^\circ} = \frac{f}{P^\circ}$	The definition for the activity of a gas, in terms of a <b>fugacity constant</b> $\phi$ . $f = \phi P$ is known as the <b>fugacity</b> and has dimensions of pressure. <b>Activity</b> is a dimensionless quantity, so must be divided by the standard pressure $P^\circ$ . The fugacity constant is also unitless, and functions as a collection of non-idealities for a real gas. As $P \rightarrow 0$ , real gases behave more like ideal and $\phi \rightarrow 1$ .
Standard States	<p><b>Standard states</b> are arbitrary reference points which are defined depending on the type of system. When systems are in their standard state, their activity <math>a = 1</math> by definition.</p> <ul style="list-style-type: none"> <li>• Ideal gases: <math>a = \frac{P}{P^\circ}</math> so <math>a = 1</math> when <math>P = P^\circ = 1 \text{ atm}</math></li> <li>• Real gases: <math>a = \frac{\phi P}{P^\circ}</math> so <math>a = 1</math> when <math>\phi P = P^\circ = 1 \text{ atm}</math>.</li> <li>• Pure liquids and solids: <math>a = 1</math> for pure liquids and solids at 1 atm by convention.</li> <li>• Solute in an ideal solution: <math>a = \frac{c}{c^\circ}</math> where <math>c^\circ = 1 \text{ mol L}^{-1}</math>. So <math>a = 1</math> when <math>c = c^\circ</math>.</li> <li>• Solute in a non-ideal solution: <math>a = \frac{\gamma c}{c^\circ}</math> where <math>\gamma</math> is known as the <b>activity coefficient</b>, similar to a fugacity coefficient but for solutions.</li> <li>• Solvent in an ideal solution: <math>a = 1</math> for pure solvents and <math>a = x</math> where <math>x</math> is the mole fraction in solvent mixtures.</li> <li>• Solvent in a non-ideal solution: <math>a = \gamma x</math> where <math>\gamma</math> is the activity coefficient of the solvent.</li> </ul>

## 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<sub>3</sub>COOH and 25 mL of 0.50 M CH<sub>3</sub>COONa.  $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$

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

- HCl:  $0.10 \text{ mol L}^{-1} \times 0.010 \text{ L} = 0.001 \text{ mol}$
- CH<sub>3</sub>COOH:  $1.0 \text{ mol L}^{-1} \times 0.025 \text{ L} = 0.025 \text{ mol}$
- CH<sub>3</sub>COONa:  $0.50 \text{ mol L}^{-1} \times 0.025 \text{ L} = 0.0125 \text{ mol}$

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<sub>3</sub>COONa into CH<sub>3</sub>COO<sup>-</sup> (a weak base) and Na<sup>+</sup> (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 <sub>3</sub> COO <sup>-</sup>	→	Cl <sup>-</sup>	+	CH <sub>3</sub> COOH
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  $10 \geq \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \geq 0.1$ , then the solution is a buffer. Since volumes cancel out, we can use the number of moles or the concentration.

- $\frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{0.026 \text{ mol}}{0.0115 \text{ mol}} = 2.26$ .

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.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right) \\ &= -\log_{10} (1.8 \times 10^{-5}) + \log_{10} \left( \frac{0.0115 \text{ mol}}{0.026 \text{ mol}} \right) \\ &= 4.39 \end{aligned}$$

For buffer solutions, the pH should always be within  $\pm 1$  of the  $\text{p}K_a$  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. This is just the acid dissociation reaction of a unspecified weak acid  $HA$  with water,



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

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

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

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

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

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

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

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

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  $1 \times 10^{-5} \text{ mol L}^{-1}$ ) 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

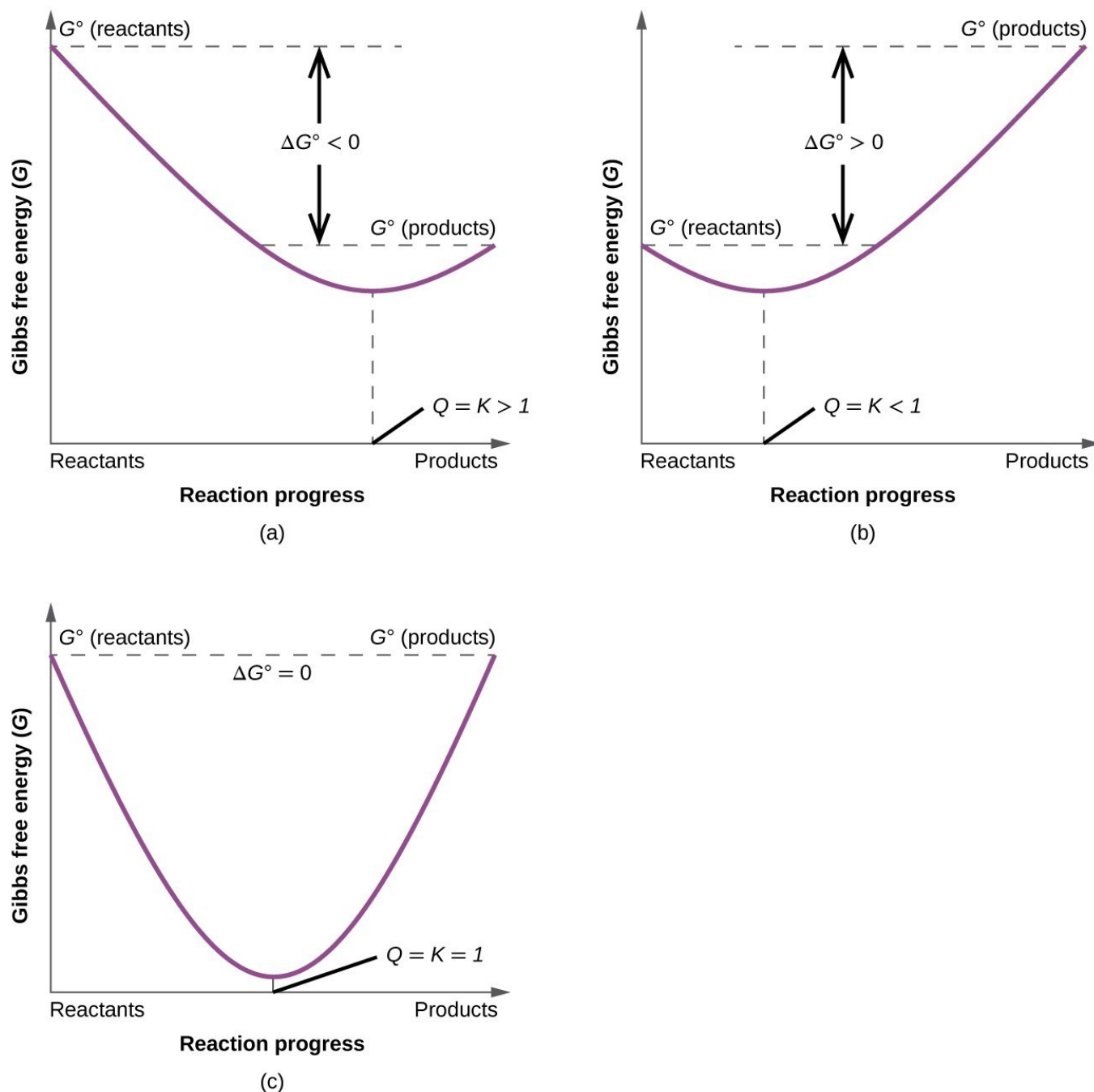


Figure 1: These useful figures<sup>1</sup> show the Gibbs free energy of a hypothetical reaction that goes from 100% pure reactants in their standard state on the left to 100% pure products in their standard state on the right. As the reaction mixture changes from 0% products to 100% products, the Gibbs free energy of the reaction mixture changes accordingly. The corresponding reaction progress at minimized standard Gibbs 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)**  $G^\circ(\text{reactants})$  is higher than  $G^\circ(\text{products})$ . In this case, we see that the  $\Delta G^\circ$  is negative, and at equilibrium there will be a greater proportion of products than reactants. **(b)**  $G^\circ(\text{products})$  is higher than  $G^\circ(\text{reactants})$ . In this case,  $\Delta G^\circ$  is positive and the reaction mixture favours reactants at equilibrium. **(c)**  $G^\circ(\text{products}) = G^\circ(\text{reactants})$ , 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.

<sup>1</sup>Taken From: <https://courses.lumenlearning.com/suny-mcc-chemistryformajors-2/chapter/free-energy/>

# Thermodynamics of Electrochemical Cells

Equation/Concept	Info About Equation/Concept
Electrochemical Cell	An <b>electrochemical cell</b> is a setup that includes two <b>electrodes</b> placed into an <b>electrolyte solution</b> . A <b>half cell</b> is a single electrode in electrolyte solution.
$\varepsilon_{cell}$	The <b>electromotive force</b> (emf) or <b>cell potential</b> (measured in volts) is the electrical potential produced by an electrochemical cell.
$V_{EC} = \varepsilon_{cell} - \sum_i IR_i$	The measured potential difference of an electrochemical cell $V_{EC}$ will generally not be the same as the emf $\varepsilon_{cell}$ because each internal resistance $R_i$ in the circuit will reduce the measured voltage by $IR_i$ , where $I$ is the current which flows through the circuit via an irreversible process (a spontaneous chemical reaction). To properly measure $\varepsilon_{cell}$ , a reversible measurement must be made by preventing current from flowing ( $I \rightarrow 0$ ). This type of measurement can be achieved using a potentiometer circuit, which exactly balances $\varepsilon_{cell}$ with a known standard voltage, preventing current from flowing.
$(\delta G)_{T,P} = w_{net,rev} = w_{net,max}$	Under constant $T$ and $P$ conditions, the decrease in Gibbs free energy is equal to the maximum possible (i.e. reversible) non- $PV$ work ( $w_{net}$ ) done by the system on the surroundings.
$w_{net} = Q\varepsilon = Ne\varepsilon = -nF\varepsilon$	The definition of <b>electrical work</b> . $Q$ (units of Coulombs $C$ ) is the charged which passes through a circuit, and $\varepsilon$ (units of $J C^{-1}$ ) is the potential difference (voltage) across the circuit, which is just the cell emf if the voltage difference is produced by an electrochemical cell. The total charge can be written in terms of the number of electrons $N$ times the elementary electron charge $e$ , or as the number of moles of electrons $n$ times the total electric charge of a mole of electrons (a Faraday) $F$ .
$(\Delta G)_{T,P} = -nF\varepsilon$	At constant pressure, we can write the change in Gibbs free energy in terms of moles of electrons passed in a circuit times the circuit voltage drop.
$\varepsilon = \varepsilon^\circ - \frac{RT}{nF} \ln Q_a$	The <b>Nernst Equation</b> . This equation applies under constant $T$ and $P$ conditions only. Derived from the expression for differences in Gibbs free energy by replacing $\Delta G = -nF\varepsilon$ and $\Delta G^\circ = -nF\varepsilon^\circ$ . Here $\varepsilon^\circ$ is the emf of an electrochemical cell under standard state conditions (i.e. $P = 1$ bar, $C = 1$ mol $L^{-1}$ ). Using this equation we can calculate the emf of a given cell by using a tabulated $\varepsilon^\circ$ and a calculated reaction quotient $Q_a$ , which is specific to the electrochemical cell of interest.
$\varepsilon = \varepsilon^\circ - \left(\frac{0.0257 \text{ V}}{n}\right) \ln Q_a$	A simplified version of the Nernst Equation for use when $T = 25^\circ C$ .
$\frac{d\Delta G}{dT} = -\Delta S = -nF \frac{d\varepsilon}{dT}$	An equation for the temperature dependence of a cell emf, assuming that $\Delta S$ and $\Delta H$ are both independent of temperature.
$\varepsilon = 0, \quad \varepsilon^\circ = \frac{RT}{nF} \ln K_{eq}$	A link between the standard cell potential and its equilibrium constant. The first equation gives one a condition for electrochemical equilibrium.
Sign of $\varepsilon$	Its important to remember that the sign convention for $\varepsilon$ is <b>opposite</b> that of $\Delta G$ . Therefore, when $\varepsilon > 0$ the forward reaction is spontaneous under the given reaction conditions.



Equation/Concept	Info About Equation/Concept
$\text{Zn}_{(s)} \mid \text{Zn}_{(aq)}^{2+} \parallel \text{Cu}_{(aq)}^{2+} \mid \text{Cu}_{(s)}$	By convention, electrochemical cells are written with the <b>oxidation reaction</b> on the <b>left hand electrode</b> (LHE) half-cell (e.g. $\text{Zn}_{(s)} \rightleftharpoons \text{Zn}_{(aq)}^{2+} + 2e^-$ ) and the <b>reduction reaction</b> written on the <b>right hand electrode</b> (RHE) half-cell (e.g. $\text{Cu}_{(aq)}^{2+} + 2e^- \rightleftharpoons \text{Cu}_{(s)}$ ). A single bar ( ) represents a phase boundary, while two bars (  ) represents a separation of the two half cells, and the presence of a salt bridge to prevent charge accumulation.
Anode	An anode is defined as the <b>positively charged electrode</b> which electrons <b>leave</b> from.
Cathode	A cathode is defined as the <b>negatively charged electrode</b> which electrons <b>enter</b> .
$\varepsilon_{\text{cell}} = \varepsilon_{\text{red}}(\text{RHE}) - \varepsilon_{\text{red}}(\text{LHE})$	Since the RHE is defined as the reduction reaction in an electrochemical cell by convention, the LHE reaction of interest is actually the oxidation reaction which has $\varepsilon$ equal and opposite to its reduction reaction. The full emf of the cell is simply the sum of the emf of both half reactions. Half cell reduction $\varepsilon$ are tabulated by comparison with the <b>standard hydrogen electrode (SHE)</b> (which has $\varepsilon^\circ = 0 \text{ V}$ by definition), so are more convenient to use than oxidation potentials.

## Colligative Properties

Equation/Concept	Info About Equation/Concept
The four colligative properties.	<p>The four colligative properties are:</p> <ul style="list-style-type: none"> <li>• Vapour pressure lowering</li> <li>• Boiling point elevation</li> <li>• Freezing point depression</li> <li>• Osmotic pressure</li> </ul> <p>All colligative properties depend on the chemical properties of the <b>solvent</b>, but not the <b>solute</b>. Colligative properties only depend on the <b>number of dissolved particles</b>. Note that ionic compounds often dissolve into multiple ions in solution, all of which will contribute to colligative properties.</p>
Cause of colligative properties	Colligative properties can be described as a modification of the free energy of the liquid solvent by the presence of the solute. Colligative properties are all <b>entropically driven</b> (caused by an increase in overall system entropy), but may be enhanced or reduced by <b>enthalpic</b> effects in real solutions.
$G_{\text{solv}} = G_{\text{solv}}^\circ + RT \ln a_{\text{solv}}$	This equation is used to describe the extent of colligative properties. When solvents are pure, $a_A \equiv 1$ by definition, so $G_{\text{solv}} = G_{\text{solv}}^\circ$ . A solvent's activity $a_{\text{solv}} = x_{\text{solv}}$ for ideal (dilute) solutions, where $x_{\text{solv}} = \frac{n_{\text{solv}}}{n_{\text{solv}} + \sum_i n_i}$ is the solvent's mole fraction of the solution. Whenever any solutes are present $a_{\text{solv}} < 1$ so $G_{\text{solv}} < G_{\text{solv}}^\circ$ . This reduction in Gibbs free energy is linked to all four colligative properties.
$\ln x_{\text{solv}} = \frac{\Delta H_{\text{vap}}^\circ}{R} \left( \frac{1}{T} + \frac{1}{T_0} \right)$	This equation is true for <b>ideal dilute solvents</b> with mole fraction $x_{\text{solv}}$ in solution. $\Delta H_{\text{vap}}^\circ$ is assumed to be independent of $T$ .

Equation/Concept	Info About Equation/Concept
$\Delta T_{BP} \approx \frac{RT_{BP}^2 x_B}{\Delta H_{vap}^\circ}$	<p>This equation approximates the boiling point elevation due to colligative properties. <math>x_B</math> is the mole fraction of all dissolved solutes. It makes the following assumptions:</p> <ul style="list-style-type: none"> <li>• <math>\Delta H_{vap}^\circ</math> is independent of <math>T</math> in the neighbourhood of the normal boiling temperature.</li> <li>• <math>\ln x_{solv} \approx x_B</math> which is mathematically justified when <math>x_B \ll 1</math>.</li> <li>• <math>T'_{BP} \times T_{BP} \approx T_{BP}^2</math> where <math>T'_{BP}</math> is the new boiling point after colligative effects. This is a small approximation for small boiling point shifts.</li> </ul> <p>This equation can also be used to describe freezing point depression by switching <math>T_{BP}</math> for <math>T_{FP}</math> and <math>\Delta H_{vap}^{circ}</math> for <math>\Delta H_{fus}^{circ}</math>.</p>
Semi-permeable membrane	A semi-permeable membrane allows some materials to freely pass through, but blocks others based on charge, molecular size, or some other chemical characteristic.
$-RT \ln x_{solv} = \Pi V_{solv}$	This equation assumes that $a_{solv} = x_{solv}$ , which is fairly accurate for <b>dilute solutions</b> , and true exactly for ideal-dilute solutions. The equation is also derived by assuming that the <b>volume of the solution is independent of pressure</b> . This is more-or-less true for liquids at normal pressures. $\Pi = P^\circ - P$ is the osmotic or hydrostatic pressure.
$\Pi V = n_B RT$	Known as the <b>van't Hoff osmotic pressure equation</b> . Derived from the previous equation by use of two approximations: (1) $-\ln x_{solv} = -\ln(1-x_B) \approx x_B$ and (2) $x_B = \frac{n_B}{n_{solv} + n_B} \approx \frac{n_B}{n_{solv}}$ . Both approximations are valid only for dilute solutions, where $x_{solv} \gg x_B$ .
$\Pi = \Delta c RT$	The van't Hoff osmotic pressure equation for use when both sides of a semi-permeable membrane have different non-zero concentrations of solute. $\Delta c$ is the difference in concentration between sides.

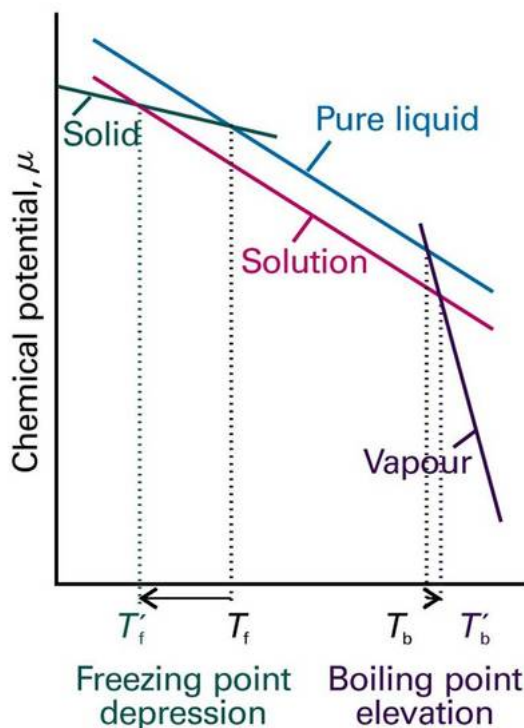


Figure 5-21  
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Figure 2: A diagram showing the lowering of the chemical potential (Gibbs free energy) of an ideal solvent liquid phase by colligative properties (lowering by  $RT \ln x_A$ ). Notice that the lowering of the chemical potential lowers the melting point much more than it elevates the boiling point. Note that lowering the boiling point necessarily reduces the solvent vapour pressure, as the boiling point is simply the point where the vapour pressure of the solvent equals that of the surroundings.

# 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 $\text{Rate} = k[A]^a[B]^b$ 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.
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 <i>and</i> lowers the activation energy of a reaction. Living creatures contain countless protein-based catalysts called <b>enzymes</b> 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 $a[A] \rightarrow b[B]$ . 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 $A \rightarrow bB$ .
$\text{Rate} = -b \frac{d[A]}{dt} = k[A]$	The differential rate law for a first order reaction $A \rightarrow bB$ . Often the rate constant $k$ will include the factor of $\frac{1}{b}$ .

Equation/Concept	Info About Equation/Concept
$[A](t) = [A]_0 e^{-kt}$	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 $2A \rightarrow bB$ .
Rate $= -\frac{b}{2} \frac{[A]}{dt} = k[A]^2$	The differential rate law for a first order reaction $A \rightarrow bB$ . 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).
$k = Ae^{-\frac{E_a}{RT}}$	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 $E + S \xrightleftharpoons[k_{-1}]{k_1} ES \xrightarrow{k_{\text{cat}}} E + P$ . Here, $K_M = \frac{[E][S]}{[ES]} = \frac{k_{-1} + k_{\text{cat}}}{k_1}$ 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 $[S]$ .

## Reaction Coordinate Diagrams

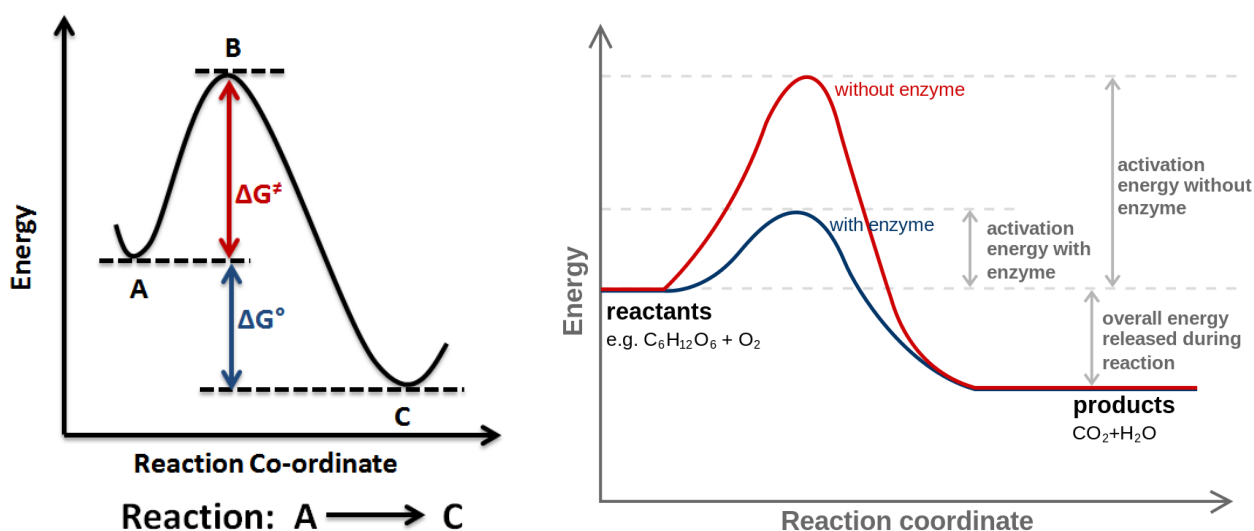


Figure 3: **(Left)** A diagram of Gibbs free energy vs reaction coordinate for an elementary reaction. In this context, the reaction coordinate refers to the point along the reaction pathway from reactant to product that requires the lowest raise in free energy. It is easy to imagine a multitude of potential 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.<sup>2</sup>

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  $1 \times 10^{-10}$  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 ( $\ddagger$ ). 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.

### Free Energy vs Reaction Progress

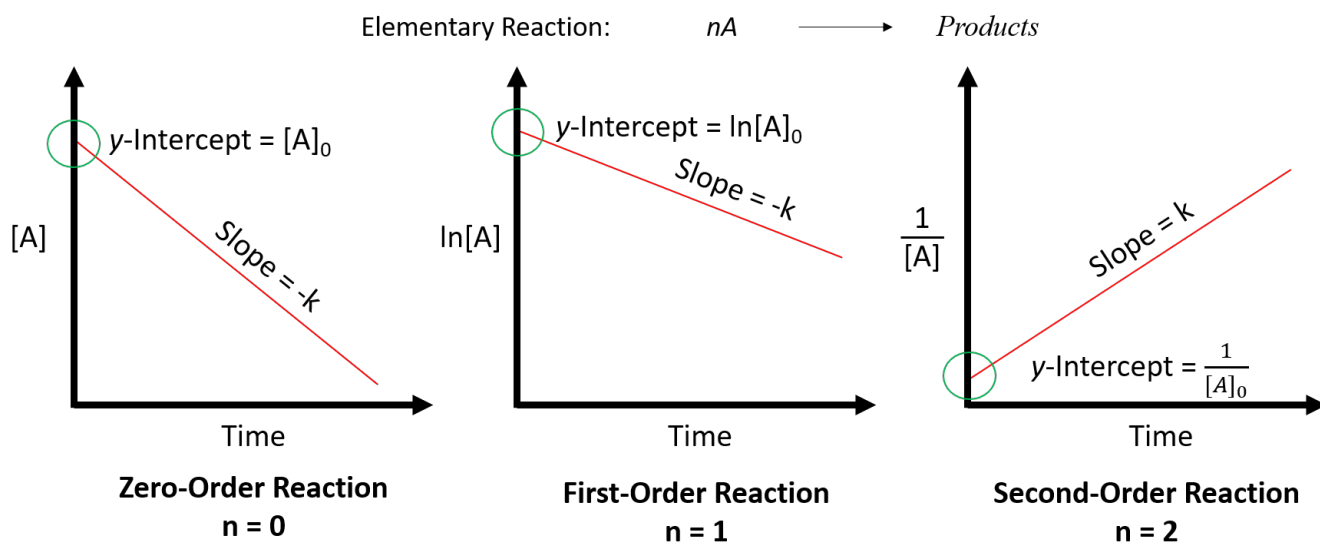


Figure 4: How we can use plots of concentration vs time to determine the order of a reaction with respect to a particular reactant. Only one of the above plots should be linear with respect to a particular reactant involved in a reaction. Find the linear plot to determine the reaction order. The reaction order is *also* the stoichiometric coefficient if the reaction is elementary.

<sup>2</sup>Left: [http://www.wikiwand.com/en/Energy\\_profile\\_\(chemistry\)](http://www.wikiwand.com/en/Energy_profile_(chemistry)) Right: [https://en.wikipedia.org/wiki/Reaction\\_coordinate](https://en.wikipedia.org/wiki/Reaction_coordinate)

# 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:



- $E$  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  $E + P \rightarrow ES$  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

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

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

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

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

$$\frac{d[ES]}{dt} = 0. \quad (10)$$

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

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

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

$$V_0 = k_{cat}[ES]. \quad (12)$$

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

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

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,

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

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

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

**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

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

This gives us the limiting behaviour

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

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

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

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

## Converting Between Equilibrium Constants and Percentages:

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



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

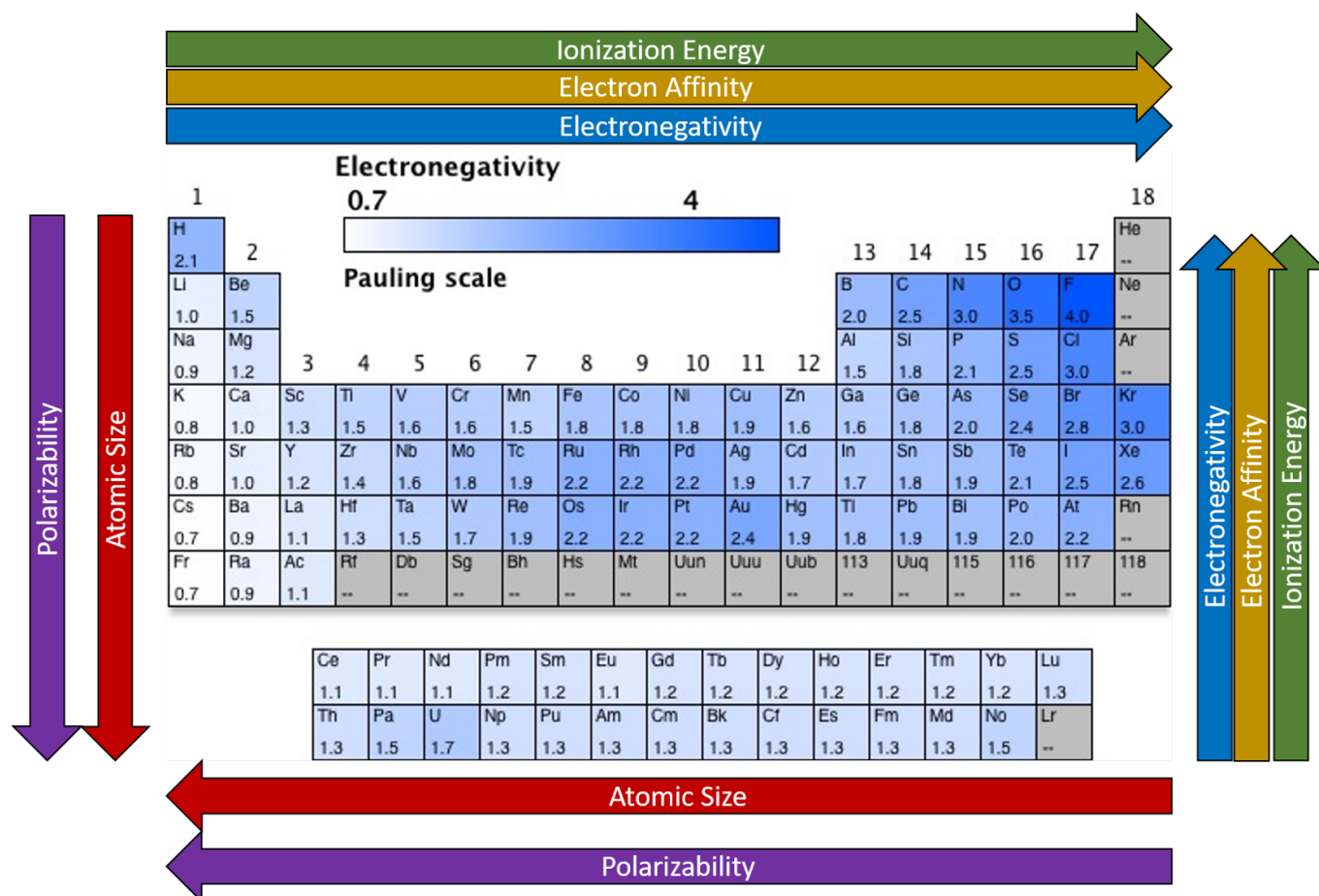
$$\chi_B = \frac{\frac{[B]}{[A]}}{\frac{[A]}{[A]} + \frac{[B]}{[A]}} = \frac{K}{1 + K}$$

and

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

# Physical Constants and Periodic Trends (for Reference)

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





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# Equations and Constants

(note: conditions for applying equations are not specified)

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$k = 1.3807 \times 10^{-23} \text{ J K}^{-1}$$

$$N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$$

$$F = 96485 \text{ C mol}^{-1}$$

$$0^\circ \text{C} = 273.15 \text{ K}$$

$$1 \text{ atm} = 101325 \text{ Pa}$$

$$1 \text{ L} = 0.001 \text{ m}^3$$

$$1 \text{ L atm} = 101.325 \text{ J}$$

$$PV = nRT$$

$$\left( P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

$$\Delta U = U_2 - U_1 = q + w$$

$$dw = -P_{\text{ex}} dV$$

$$w = -P_{\text{ex}} (V_2 - V_1)$$

$$w = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$dq = C \cdot dT$$

$$C_V = nC_{V,m} = \frac{dq_V}{dT}$$

$$\Delta U = q_V = \int_{T_1}^{T_2} nC_{V,m} dT = \int_{T_1}^{T_2} C_V dT$$

$$H = U + PV$$

$$C_P = nC_{P,m} = \frac{dq_P}{dT}$$

$$\Delta H = q_P = \int_{T_1}^{T_2} nC_{P,m} dT = \int_{T_1}^{T_2} C_P dT$$

$$\Delta H_{\text{rxn}}^0 = \sum_i \nu_i \Delta H_{m,i}^0 (\text{products}) - \sum_j \nu_j \Delta H_{m,j}^0 (\text{reactants})$$

$$C_{V,m} = \frac{3}{2} R, \quad C_{P,m} = \frac{5}{2} R$$

$$dS = dq_{\text{rev}} / T$$

$$\Delta S = S_2 - S_1 = \int_{\text{state 1}}^{\text{state 2}} \frac{dq_{\text{rev}}}{T}$$

$$(\Delta S)_{T,P} = \Delta H / T$$

$$(\Delta S)_T = nR \ln \left( \frac{V_2}{V_1} \right) = nR \ln \left( \frac{P_1}{P_2} \right)$$

$$(\Delta S)_V = nC_{V,m} \ln \left( \frac{T_2}{T_1} \right)$$

$$(\Delta S)_P = nC_{P,m} \ln \left( \frac{T_2}{T_1} \right)$$

$$\Delta S = nC_{V,m} \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S = nC_{P,m} \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{P_1}{P_2} \right)$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\ln \left( \frac{P_2}{P_1} \right) = \frac{-\Delta H_{\text{vap},m}^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{-\Delta H_{\text{rxn}}^0}{(1 \text{ mol}) \cdot R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$F = C - P + 2$$

$$G = H - TS$$

$$\Delta G_{T,P} = -T \cdot \Delta S_{\text{univ}}$$

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + (1 \text{ mol}) \cdot RT \ln Q$$

$$\Delta G_{\text{rxn}}^0 = -(1 \text{ mol}) \cdot RT \ln K$$

$$\Delta G_{\text{rxn}} = -nF\varepsilon, \quad \Delta G_{\text{rxn}}^0 = -nF\varepsilon^0$$

$$\varepsilon = \varepsilon^0 - \frac{(1 \text{ mol}) \cdot RT}{nF} \ln Q$$

$$\Delta T_b = T_{\text{b,mix}} - T_{\text{b,pure}} \approx K_b b_B$$

$$\Delta T_f = T_{\text{f,mix}} - T_{\text{f,pure}} \approx -K_f b_B$$

$$\Pi = c_B RT$$

$$\Delta \Pi = \Delta c \cdot RT$$

$$\varepsilon \approx \frac{-RT}{z_l F} \ln \left( \frac{[i]_{\text{R}}}{[i]_{\text{L}}} \right)$$

$$T = \frac{I}{I_0}$$

$$A = -\log_{10} T = lc\varepsilon$$

$$\nu = k[A]^a [B]^b [C]^c \dots$$

$$aA \rightarrow B: \quad \nu = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n$$

$$aA \rightarrow B: \quad [A] = [A]_0 - akt, \quad t_{1/2} = \frac{[A]_0}{2ak}$$

$$aA \rightarrow B: \quad \ln \left( \frac{[A]}{[A]_0} \right) = -akt, \quad t_{1/2} = \frac{\ln 2}{ak}$$

$$aA \rightarrow B: \quad \frac{1}{[A]} - \frac{1}{[A]_0} = akt, \quad t_{1/2} = \frac{1}{ak[A]_0}$$

$$t = \frac{t_{1/2}}{\ln 0.5} \ln \left( \frac{[A]}{[A]_0} \right), \quad \frac{[A]}{[A]_0} = 0.5^{\frac{\text{time}}{\text{half-life}}}$$

$$K = \frac{k_1}{k'_1} \times \frac{k_2}{k'_2} \times \frac{k_3}{k'_3} \times \dots$$

$$k = A e^{\frac{-E_a}{RT}} = A \exp \left( \frac{-E_a}{RT} \right)$$

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

$$\nu = \frac{[S] \cdot \nu_{\text{max}}}{[S] + K_M}, \quad \nu_{\text{max}} = k_b [E]_{\text{tot}}$$

## Useful Spectroscopic Data

IR Modes of Vibrational Frequency	
Vibration	$\nu$ (cm <sup>-1</sup> )
C–C stretch, bend	700–1250
C–H stretch	2850–3100 (strong)
C–H bend	1340–1465
C=C stretch	1620–1680
C=O stretch	1600–1850 (strong)
C≡C stretch	2100–2260
C≡N stretch	2100–2300
O–H stretch	3590–3650 (strong)
C=N stretch	2215–2275
N–H stretch	3200–3500 (strong)
Hydrogen-bonds	3200–3570 (broad)

Selected Isotopes & Their Masses		
Isotope	Natural Abundance	Mass
<sup>1</sup> H	99.98%	1.00783
<sup>12</sup> C	98.9%	12.0000
<sup>13</sup> C	1.1%	13.0034
<sup>14</sup> N	99.6%	14.0031
<sup>16</sup> O	99.8%	15.9949
<sup>19</sup> F	100.0%	18.9984
<sup>35</sup> Cl	75.8%	34.9689
<sup>37</sup> Cl	24.2%	36.9659
<sup>79</sup> Br	50.7%	78.9183
<sup>81</sup> Br	49.3%	80.9163
<sup>127</sup> I	100.0%	126.904

Common Fragments & Their Masses	
Fragment	Mass
CH <sub>3</sub>	15
CH <sub>2</sub> CH <sub>3</sub>	29
HC(=O)	29
HOCH <sub>2</sub>	31
CH <sub>3</sub> C(=O)	43
HOC(=O)	45

UV-Visible Absorption Bands	
Chromophore	$\lambda_{\text{max}}$ (nm)
C=O (carbonyl ketones, aldehydes, esters)	250–350 (weak)
CH=CH–CH=O (conjugated carbonyl)	200–300 (strong) and 300–400 (weak)
C=C (alkenes and conjugated alkenes)	160–340 (strong)
Benzene and derivatives	200–300 (moderate–strong)

<sup>1</sup> H NMR Downfield Shifts from TMS	
Type of Proton <sup>1</sup> H	Chemical Shift $\delta$
RCH <sub>3</sub>	0.8 – 1.0
RCH <sub>2</sub> R	1.2 – 1.4
R <sub>3</sub> CH	1.4 – 1.7
R <sub>2</sub> C=C(R)–CH <sub>3</sub>	1.6 – 1.9
ArCH <sub>3</sub> (Ar is benzene ring)	2.2 – 2.5
RCH <sub>2</sub> Cl	3.6 – 3.8
RCH <sub>2</sub> Br	3.4 – 3.6
RCH <sub>2</sub> I	3.1 – 3.3
ROCH <sub>2</sub> R	3.3 – 3.9
RCH <sub>2</sub> OH	3.3 – 4.0
RC(=O)CH <sub>3</sub>	2.1 – 2.6
RC(=O)H	9.5 – 9.6
R <sub>2</sub> C=CH <sub>2</sub>	4.6 – 5.0
R <sub>2</sub> C=C(R)H	5.2 – 5.7
ArH	6.0 – 9.5
RC≡CH	2.5 – 3.1
ROH	0.5 – 6.0
RC(=O)OH	10 – 13
ArOH	4.5 – 7.7
R–NH <sub>2</sub>	1.0 – 5.0

<sup>13</sup> C NMR Chemical Shift Ranges	
Group	<sup>13</sup> C Shift $\delta$
TMS	0.0
–CH <sub>3</sub> (with only H or R at C <sub>α</sub> or C <sub>β</sub> )	0 – 30
–CH <sub>2</sub> (with only H or R at C <sub>α</sub> or C <sub>β</sub> )	20 – 45
–CH (with only H or R at C <sub>α</sub> or C <sub>β</sub> )	30 – 60
C quaternary (with only H or R at C <sub>α</sub> or C <sub>β</sub> )	30 – 50
O–CH <sub>n</sub> (n = 0–3)	50 – 80
N–CH <sub>n</sub> (n = 0–3)	15 – 70
C≡C	75 – 95
C=C	105 – 145
C(aromatic)	110 – 155
C(heteroaromatic)	105 – 165
–C≡N	115 – 125
C=O (acids, esters, amides)	155 – 185
C=O (aldehydes, ketones)	185 – 225

Mathematical Relations

$\pi = 3.141\ 592\ 653\ 59 \dots$        $e = 2.718\ 281\ 828\ 46 \dots$

Logarithms & Exponentials

$\ln(x) + \ln(y) = \ln(xy)$   
 $a \ln(x) = \ln(x^a)$   
 $e^x e^y = e^{x+y}$   
 $(e^x)^a = e^{ax}$

$\ln(x) - \ln(y) = \ln(x/y)$   
 $\ln(x) = \ln(10) \cdot \log(x)$   
 $e^x / e^y = e^{x-y}$   
 $e^{-a} = 1/e^a$

Taylor Expansions

$$f(x) = \sum_{n=0}^{\infty} \frac{(x-a)^n}{n!} \left( \frac{d^n f}{dx^n} \right)_{x=a}$$
$$e^x = 1 + x + \frac{1}{2}x^2 + \dots$$
$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \dots$$

$$\ln(x) = (x-1) - \frac{1}{2}(x-1)^2 + \frac{1}{3}(x-1)^3 - \frac{1}{4}(x-1)^4 + \dots$$
$$\frac{1}{1+x} = 1 - x + x^2 + \dots$$

Derivatives

$$d(f+g) = df + dg$$
$$d\left(\frac{f}{g}\right) = \frac{g \cdot df - f \cdot dg}{g^2}$$
$$\frac{dx^n}{dx} = nx^{n-1}$$

$$d(f \cdot g) = f \cdot dg + g \cdot df$$
$$\frac{df}{dx} = \frac{df}{dg} \cdot \frac{dg}{dx}$$
$$\frac{d}{dx} e^{ax} = ae^{ax}$$

$$\frac{d}{dx} \ln(x) = \frac{1}{x}$$

Integrals

$$\int x^n dx = \frac{x^{n+1}}{n+1} + C$$
$$\int dx = x + C$$

$$\int \frac{1}{x} dx = \ln(x) + C$$
$$d \int dx = dx$$

$$\int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$
$$\int_a^b dx = x|_a^b = b - a$$

Prefixes

z	zepto	10 <sup>-21</sup>
a	atto	10 <sup>-18</sup>
f	femto	10 <sup>-15</sup>
p	pico	10 <sup>-12</sup>
n	nano	10 <sup>-9</sup>
μ	micro	10 <sup>-6</sup>
m	milli	10 <sup>-3</sup>
c	centi	10 <sup>-2</sup>
d	deci	10 <sup>-1</sup>
da	deca	10 <sup>1</sup>
k	kilo	10 <sup>3</sup>
M	mega	10 <sup>6</sup>
G	giga	10 <sup>9</sup>
T	tera	10 <sup>12</sup>
P	peta	10 <sup>15</sup>

Greek Alphabet

A, α	alpha	Π, π	pi
B, β	beta	Ρ, ρ	rho
Γ, γ	gamma	Σ, σ	sigma
Δ, δ	delta	Τ, τ	tau
Ε, ε	epsilon	Υ, υ	upsilon
Ζ, ζ	zeta	Φ, φ	phi
Η, η	eta	Χ, χ	chi
Θ, θ	theta	Ψ, ψ	psi
Ι, ι	iota	Ω, ω	omega
Κ, κ	kappa		
Λ, λ	lambda		
Μ, μ	mu		
Ν, ν	nu		
Ξ, ξ	xi		
Ο, ο	omicron		

# USEFUL RELATIONSHIPS

Derivatives :-

$$d x^n = n x^{n-1}$$

$$d \ln x = \frac{1}{x}$$

$$d(xy) = x dy + y dx$$

Integrals :-

$$\int x^n dx = \frac{x^{n+1}}{n+1}$$

$$\int \frac{dx}{x} = \ln x$$

Note

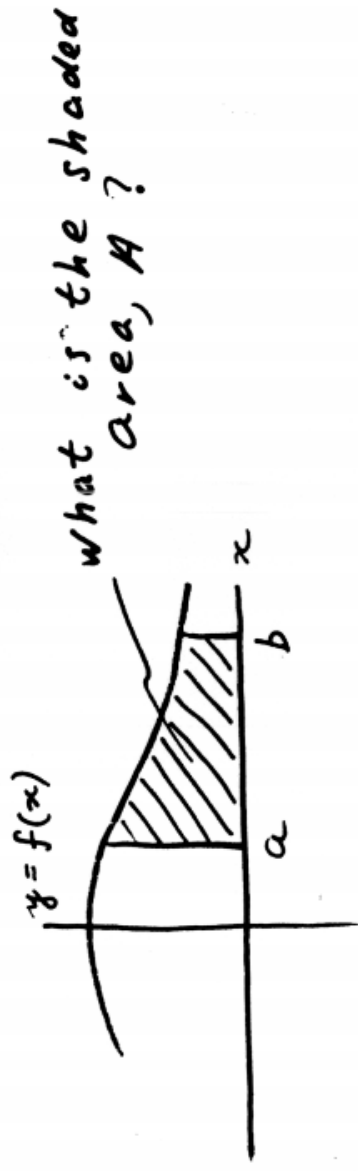
$$\int dx = x$$

$$d \int dx = dx$$

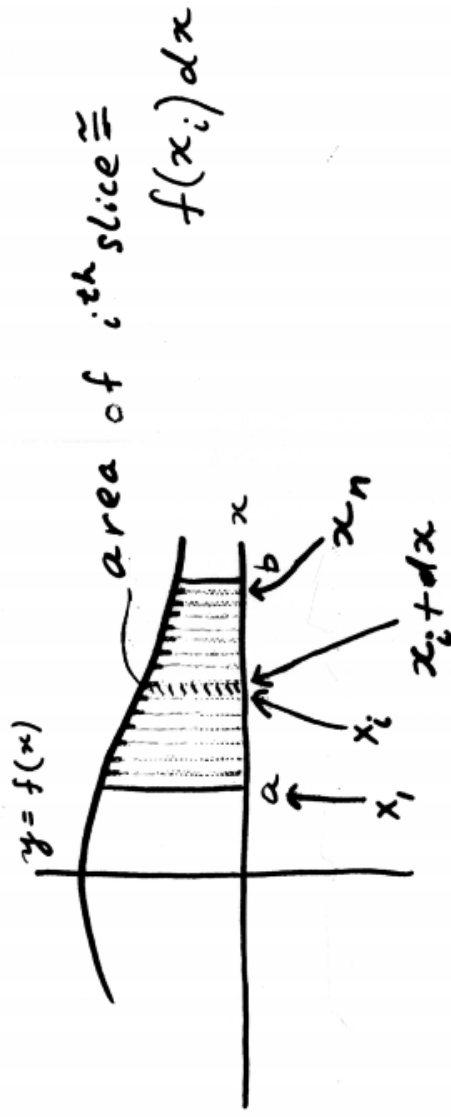
Also note

$$\int_a^b dx = x \Big|_a^b = b - a$$

# INTEGRATION



Consider  $n$  small slices of width  $dx$



Then

$$A \approx \sum_{x_i = a}^{x_i = b} f(x_i) dx$$

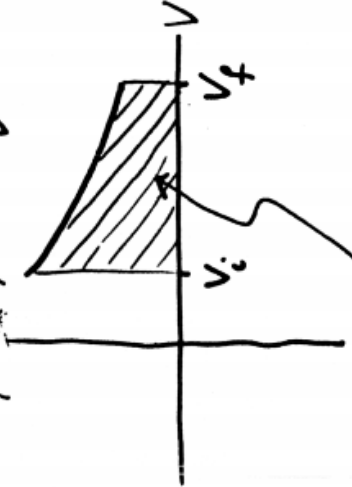
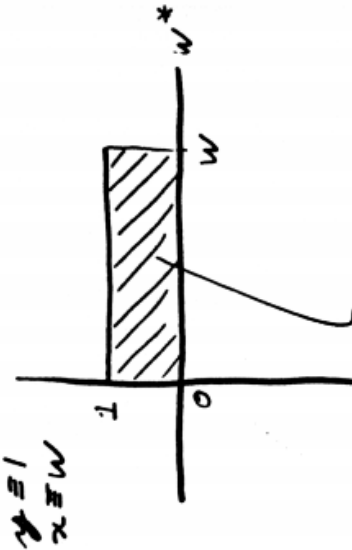
This is exact if  $dx$  is infinitesimally small. Then replace  $\sum$  by  $\int$

$$\text{Total Area} \equiv A = \int_{x=a}^{x=b} f(x) dx$$

Example:-  $-dw = PdV$  for ideal gas at const.  $T$ .

reversible

$$P = f(V) = nRT \frac{1}{V}$$



$$\text{Area} = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} nRT \frac{dV}{V}$$

$$= nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$= nRT \ln V \Big|_{V=V_i}^{V=V_f}$$

$$= nRT \ln V_f - nRT \ln V_i$$

$$= nRT \ln \left( \frac{V_f}{V_i} \right)$$

$$\text{Area} = \int_{w^*=0}^{w^*=w} dw^*$$

$$w^*=0$$

$$= w^* \Big|_{w^*=0}^{w^*=w}$$

$$= w - 0$$

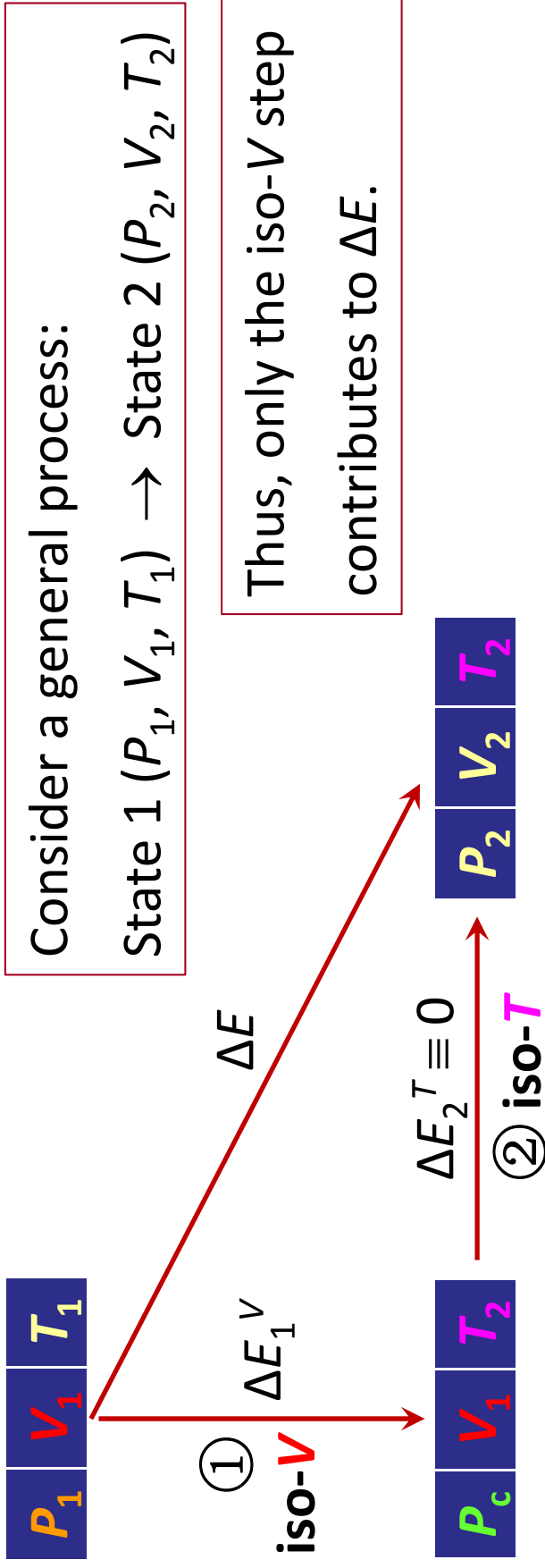
$$= w$$

$$\therefore -w = \int_{V_i}^{V_f} PdV$$

and for ideal gas at const.  $T$  + rev.

$$-w = nRT \ln \frac{V_f}{V_i}$$

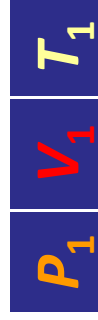
$$\Delta E = nC_{V,m} \cdot \Delta T$$



$$\left\{ \begin{array}{l} \text{The alternative process} = (1) \text{ iso-V} + (2) \text{ iso-T} \\ \Delta E = \Delta E_1^V + \Delta E_2^T \quad (\because E \text{ is a state function}) \\ \Delta E_2^T = 0 \quad (\because \text{for ideal gas, } E \text{ is a function of } T \text{ only}) \\ \Delta E = \Delta E_1^V = q_V = \int_{\text{state 1}}^{\text{state 2}} nC_{V,m} dT = nC_{V,m} \Delta T \end{array} \right.$$



$$\Delta H = nC_{P,m} \cdot \Delta T$$



①

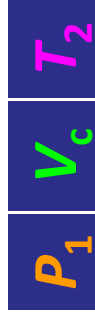
iso- $P$

$\Delta H_1^P$

$\Delta H$

$\Delta H_2^T \equiv 0$

② iso- $T$



Consider a general process:

State 1 ( $P_1, V_1, T_1$ )  $\rightarrow$  State 2 ( $P_2, V_2, T_2$ )

Thus, only the iso- $P$  step contributes to  $\Delta H$ .

The alternative process = (1) iso- $P$  + (2) iso- $T$

$\Delta H = \Delta H_1^P + \Delta H_2^T$  ( $\because H$  is a state function)

$\Delta H_2^T = 0$  ( $\because$  for ideal gas,  $H = E + PV = E + nRT$  is a function of  $T$  only)

$$\Delta H = \Delta H_1^P = q_P = \int_{\text{state 1}}^{\text{state 2}} nC_{P,m} dT = nC_{P,m} \Delta T$$