

CHEM 0330 Study Guide

Brown University

Matthew Shinkar, Nick Young, Christine Zhou

Fall 2019

0 Introduction

0.1 Forward

reticulating splines

ny

0.2 Backward

hallo spaghetti

ms

0.3 Sideways

if you have any questions, ask nick or matt lmao :)

cz

0.4 A Note

This study guide was put together to detail the material presented in Equilibrium, Rate, and Structure (CHEM 0330) taught by M. Zimmt in the Fall 2019 semester at Brown University. Before using this study guide, there are a few things that should be noted.

This study guide is meant to review key concepts taught in class and provide a workable number of examples to supplement review. It is our hope that by reading this guide, important links in thought are revitalized. However, this guide will not be comprehensive enough to supplant attending lecture or reading an actual textbook. It also may not cover every example that may appear on an exam, nor does it cover foundational material that the course expects outright. It is merely a study guide, and as such, will support, but not replace, your studying.

We recommend reviewing other class materials in conjunction with this study guide - yes, a lot of the content will overlap, but repetition is the key to mastery. Look over the class slides, board notes, textbook, Canvas quizzes, GPS files, and old midterms (from both this year and last year) for review.

Lastly, if you happen to find any mistakes in the study guide, please feel free to contact either Matt Shinkar (matthew.shinkar@brown.edu) or Nick Young (n-young@brown.edu) to get us to fix it.

Good luck on the final!

Matt Shinkar, Nick Young, Christine Zhou

0.5 Access

This study guide will be hosted in its most up-to-date form on Google Drive. [LINK]

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1 Quantum

1.1 Energy

Energy can be classified into a few categories, **kinetic** and **potential** being the main two. All kinds of energy are defined in a frame of reference, which helps ground our calculations. For example, in calculating gravitational potential energy (mgh), the distance h must be taken from some canonical “zero height”, which we usually define as the ground.

This reference point is important, as it helps us define negative potential energy. The main tenet of negative potential energy is that the lower the potential energy, the harder it is to get back up to 0. Think of two rocks in wells with different depths - it will be harder (take more energy) to extract the rock in the deeper well.

In the context of electrostatics, attraction decreases potential energy (increases the energy required to pull objects apart) and repulsion increases potential energy. Commonly, we define potential energy to be zero at infinite distance.

1.2 Waves

Waves are periodic disturbances that propagate through space. They can be used to describe light, electrons, and even matter itself. The characteristics of a wave are:

- **Node:** A position at which the value of the wave is 0.
- **Peak / trough:** A position at which the value of the wave is at a maximum / minimum.
- **Amplitude (A):** The height of a wave from its axis, equal to $\frac{(\text{Peak height} - \text{Trough height})}{2}$. Measured in m.
- **Wavelength (λ):** The distance between consecutive peaks (or troughs). Measured in m.
- **Frequency (ν):** The number of waves that pass by a specified location per second. Measured in Hz (1/s).
- **Velocity (v):** The velocity of wave propagation, equal to $\nu \cdot \lambda$. Measured in m/s.

When waves overlap, they can combine in two ways, forming **interference patterns**. If two waves at a particular point have the same sign, they will constructively interfere. Otherwise, they will destructively interfere.

- **Constructive Interference:** When waves are completely in phase (all peaks and troughs aligned), their sum has higher peaks and deeper troughs. If the two waves are equal, the amplitude will double. This occurs when $d_2 = d_1 + n\lambda$, where d_1 and d_2 are the distances traveled by the waves, λ is the wavelength, and n is an integer.
- **Destructive Interference:** When waves are exactly 180° **out of phase** (peaks of one matched with troughs of the other), their sum has lower peaks and shallower troughs. If the waves are otherwise equal, their sum will be a flat line. This occurs when $d_2 = d_1 + (m + \frac{1}{2})\lambda$, where d_1 and d_2 are the distances traveled by the waves, λ is the wavelength, and m is an integer.

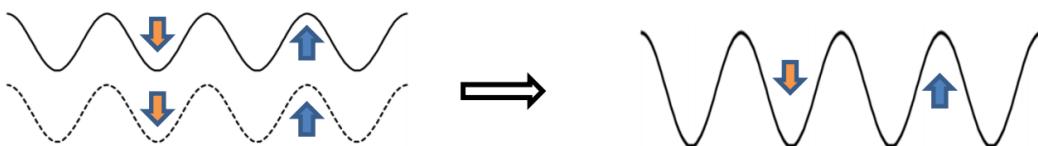


Figure 1: Constructive interference.

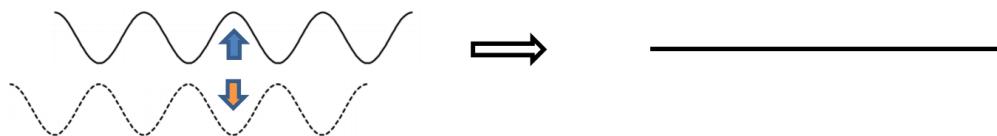


Figure 2: Destructive interference.

Light as Waves

The double-slit experiment, conducted to prove the wave-like properties of light, consists of two closely-spaced slits with a laser light shining through them. The two in-phase light sources produce an interference pattern on a screen, which looks like a series of light and dark regions. A light region is the site of constructive interference, while a dark region is the site of destructive interference.

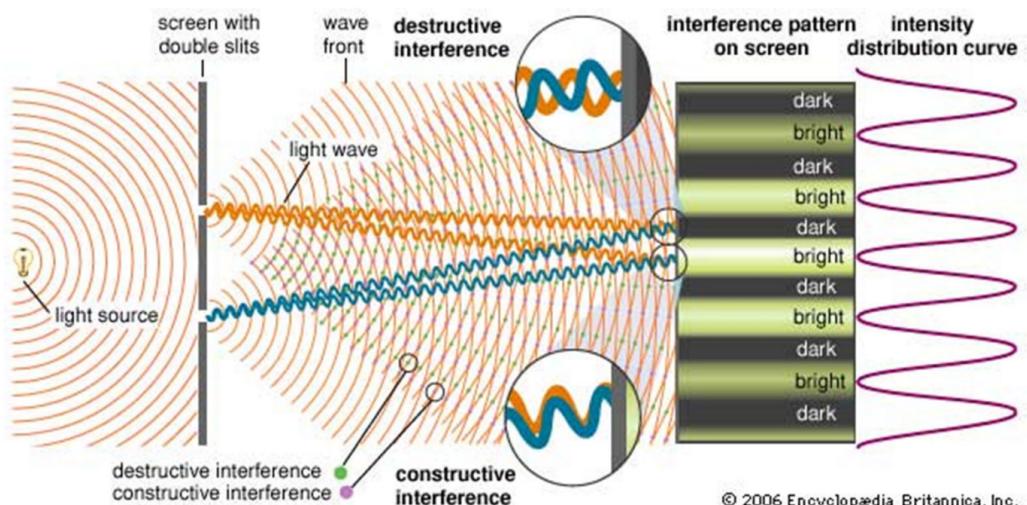


Figure 3: Double slit experiment.

Electrons as Waves

An experiment similar to the double-slit experiment was performed to prove the wave-like properties of electrons, previously thought of as particles. Instead of projecting a laser light, a stream of electrons was directed through the slits, and instead of measuring light intensity, number of electron strikes was measured on a screen. Interestingly enough, “bright spots” where a lot of electrons landed and “dark spots” where nearly no electrons landed were observed in nearly the same fashion as the interference patterns observed in the original double-slit experiment.

1.3 De Broglie's Hypothesis

De Broglie proposed a relationship between an object’s momentum and its wavelength, suggesting that all moving objects have wave-like properties.

$$\lambda_{object} = \frac{h}{mv} \quad (1)$$

Generally, the wavelengths of everyday objects are too short to measure. However, for smaller particles, like electrons, this value is much more considerable.

1.4 Electron Energy

We know that an electron's total energy can be described in terms of its kinetic and potential energy:

$$E_e = KE_e + PE_e$$

First, taking the KE :

$$\begin{aligned}\lambda_e &= \frac{h}{m_e v} \\ m_e v &= \frac{h}{\lambda_e} \\ (m_e v)^2 &= \left(\frac{h}{\lambda_e}\right)^2\end{aligned}$$

$$\boxed{\frac{1}{2}m_e v^2 = \frac{h^2}{2m_e \lambda_e^2} = KE_e} \quad (2)$$

Therefore, if you know an electron's wavelength, you know its velocity and kinetic energy.

1.5 Photoelectric Effect

Electrons can be ejected from a metal when irradiated with light - this phenomenon was coined the **photoelectric effect**. There were interesting observations about this effect's dependence on light frequency and intensity.

1. If a particular frequency of light, when shone on a piece of metal, *does* generate photoelectric current (eject electrons), the current increases linearly with light intensity.
2. Light with frequency below some minimum frequency ν_{min} generated no current, even if intensity changes.
3. Every metal has a different ν_{min} value.

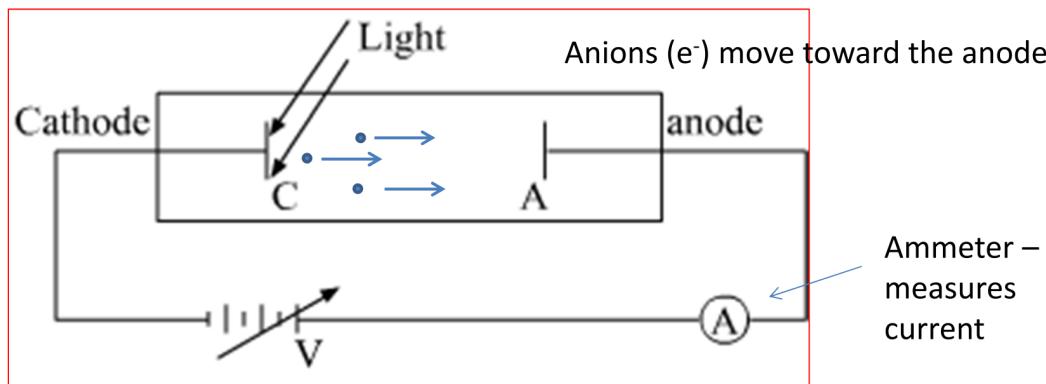


Figure 4: Photoelectric effect. Cathode: metal that ejects electrons upon illumination with light.

Einstein proposed a different view of light that stated:

1. Light is delivered in quantized packets called **photons**.
2. The energy of a photon is determined by frequency ($E_{photon} = h\nu = \frac{hc}{\lambda}$).
3. One photon must provide sufficient energy to eject one electron from the metal. This lines up with the observation of a ν_{min} .

4. Increasing intensity corresponds to increasing the number of photons.

In order to calculate the needed values, a few equations are necessary:

$$E_{photon} = h\nu = \frac{hc}{\lambda} \quad (3)$$

$$KE_{electron} = \frac{1}{2}mv^2 \quad (4)$$

We will now define the work function of a metal Φ_{metal} as the minimum energy required to eject one electron from a particular species of metal.

$$E_{photon} = \Phi_{metal} + KE_{electron} \quad (5)$$

1.6 Particle in a Box

The **particle in a box model** is a model that helps us understand the quantized nature of wave energies. Consider a box of width L containing one electron, where all positions from $x = 0$ to $x = L$ have $PE = 0$, and all positions outside the bounds of the box have $PE = \infty$. This electron can only be present within the bound of the box, since it would otherwise have infinite energy. This means that, for all permissible electron locations, all of the electron's energy is kinetic, since $PE = 0$. Therefore:

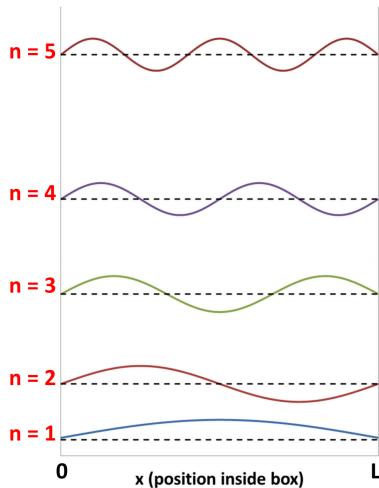
$$E_{pib} = KE_{pib} = \frac{h^2}{2m_e\lambda_e^2} = \frac{n^2h^2}{8m_eL^2} \quad (6)$$

Where:

$$\lambda_e = \frac{2L}{n} \quad (7)$$

We can represent the electron in the box as a wave. A graphical representation of the particle in a box model is shown below. As n increases, the number of nodes increases as well (# of nodes = $n - 1$). Some important observations follow:

1. The wave height at the edges is 0.
2. The wave height is highest in the middle of the box (for odd n).
3. Energy levels are quantized.
4. For each energy level (n), there is a unique wave function, Ψ (wave height shape). A higher energy level corresponds to more nodes, higher waviness, and higher KE.
5. The probability of the electron being at any position is proportional to the wave height squared (Ψ^2).

Figure 5: Particle in a box with multiple n levels.

1.7 Schrodinger's Equation

To determine the wave function, Ψ , of an electron, as well as the allowed set of energy values, **Schrodinger's Equation** is used. While the actual math is outside the scope of this course, what is important to know is that Schrodinger's equation is “fed” a function, $V(x, y, z)$, that describes its interaction with the environment, and returns exactly the set of allowed energy values and Ψ .

1.8 Absorption Spectra

When a spectrometer is used on light emitted from the sun, many wavelength are found to be missing. These gaps (absorption lines) are caused by certain particles absorbing specific wavelengths of light from sunlight, preventing them from ever reaching earth. A look at the hydrogen atom shows similar narrow, quantized absorption lines and energy levels:



Figure 6: Hydrogen Absorption Spectrum.

Why does hydrogen absorb these specific wavelengths of light? First, note that a hydrogen atom contains one proton and one electron, held together by electrostatic attraction. The Coulomb Potential (PE) is defined by:

$$PE_e = k \frac{(-q)(Z)}{r} \quad (8)$$

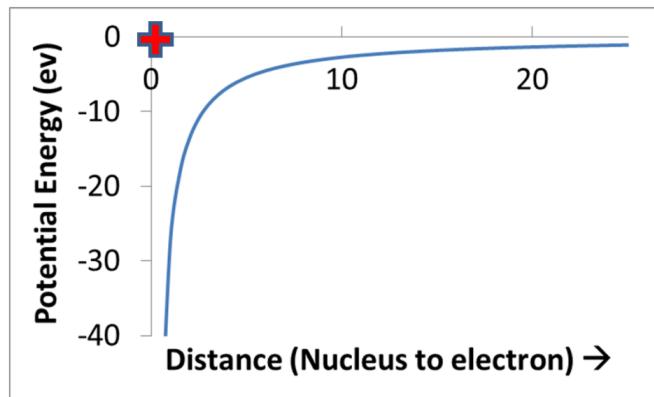


Figure 7: Distance vs. Potential Energy (H atom)

Hydrogen will absorb wavelengths of light that correspond to quantized energies of its electrons. Photons of a particular wavelength are absorbed by the hydrogen atom, exciting it.

From this equation, we know that potential energy decreases the closer the electron gets to the nuclear. If attaining the lowest possible PE determined the electron's location, then the electron would be on the nucleus - however, we know from our particle in the box model that constraining the electron to a small space increases its KE. Therefore, a balance must be struck between the two energy sources. Electron energies are *quantized*, and have wave functions describing their positional behaviour. Note that, as we move to describe wave functions for spheres, it makes more sense to describe them in terms of polar coordinates:

$$\Psi(x, y, z) \implies \Psi(r, \theta, \phi) \quad (9)$$

Where r is the distance from the nucleus to the point, θ is the angle between the z-axis and the point, and ϕ is the angle between the x-axis and the point, along the x-y plane.

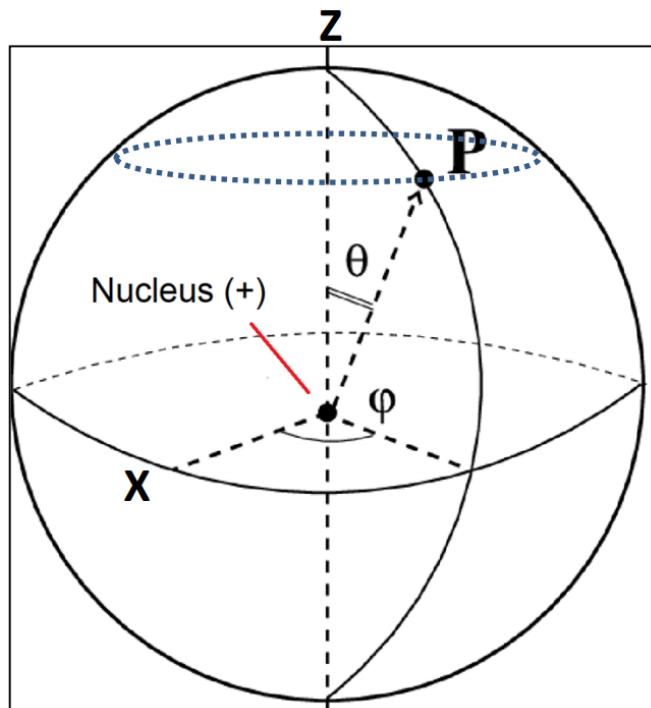


Figure 8: Polar coordinate components.

1.9 Quantum Numbers

Feeding Coulomb Potentials into Schrodinger's Equation yields energy levels and wave functions for each allowed energy level. These particular wave functions are called **atomic orbitals**, and are controlled by four **quantum numbers**:

1. n , the principle quantum number.
2. l , the angular momentum quantum number.
3. m_l , the magnetic quantum number.
4. m_s , the electron spin quantum number.

Note that, for electrons with one electron, electron energy depends only on the principle quantum number:

$$\boxed{E_n = -13.59 \text{ eV} \frac{Z^2}{n^2}} \quad (10)$$

This equation is known as **Rydberg's Equation**.

1.10 Nodes

A **radial node** is a value of r for which $\Psi = 0$, or a radius at which electron probability is zero. An **angular node** is a value of θ or ϕ where $\Psi = 0$, or an angle where electron probability is zero. These quantum numbers have physical meaning:

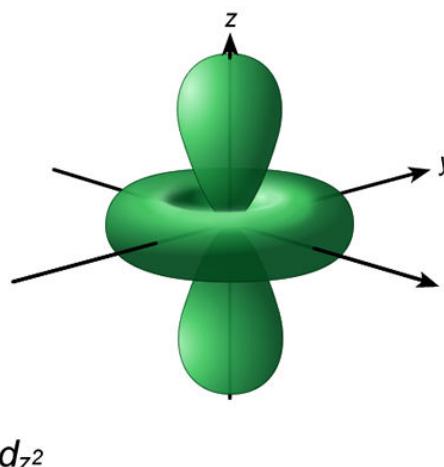
- $n - 1$ is the total number of radial and angular nodes in an orbital.
- l is the total number of angular nodes. It also determines the type of orbital (s, p, d, f).
- $|m_s|$ is the total number of nodes that overlap with the z-axis.

To get a better picture of why specific values can lead to a zero wave function value, we must understand that wave functions are the product of three formulas:

$$\boxed{\Psi(r, \theta, \phi) = F(r) G(\theta) H(\phi)} \quad (11)$$

Clearly, if $F(r) = 0$, then $\Psi = 0$. This holds for the other two formulas.

Angular nodes can manifest themselves as planar nodes, as we see quite often, but also as **conical nodes**, which is the the angle θ or ϕ at which $\Psi = 0$ is not 90° .



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Figure 9: Conical node

We saw earlier that in single-electron atoms, energy levels are determined solely by the principle quantum number, n . However, in multi-electron atoms, the angular momentum quantum number also affects energy levels. As l increases, the number of angular nodes also increases, increasing energy. Therefore:

$$\boxed{ns < np < nd < nf} \quad (12)$$

Angular Momentum

Momentum is a property of an object in translational motion. Angular Momentum is a property of an object in rotational motion. Both will stay constant unless a force is applied. Each angular node contributed $l\hbar$ to an orbital's angular momentum.

$$\boxed{L = l\hbar} \quad (13)$$

Note that this isn't \hbar , but rather \hbar or "h-bar".

1.11 Electron Energy Levels

We will look at the case of the Hydrogen atom first. An H atom's **ground state** has a $1s^1$ electron configuration - the configuration with the lowest possible energy. An H atom's **excited state** has the electron in a higher energy orbital, and has higher energy than the ground state. The first excited state has an electron configuration of $2s^1$ or $2p^1$. States can change through the absorption and emission of energy as photons. Note that, for mono-electronic atoms and ions, there is no energy difference between s orbitals, p orbitals, and other orbital shapes. In all other atoms and ions, an increase in l leads to an increase in orbital energy.

1.12 Multi-electron Atoms

We know that nucleus-electron attraction lowers electron potential energy. However, in multi-electron atoms, electron-electron repulsion *raises* electron potential energy. This means that the effective nuclear charge is less than the actual nuclear charge on outer (screened) electrons. Therefore, we must pretend that nuclear charge is lower than it actually is.

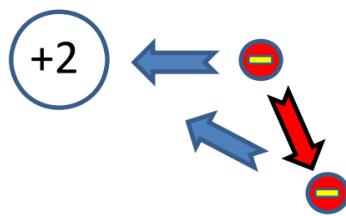


Figure 10: Electron-electron repulsion.

For multi-electron atoms, we can use the atomic orbitals defined for the H atom to describe the distribution of the multiple electrons in heavier elements. An **electron configuration** is used to describe which orbitals electrons of an atom inhabit, and are subject to a few rules:

1. At most 2 electrons can be in the same atomic orbital.
2. Electrons have a property called “spin”, characterized by m_s , which can be either $+1/2$ or $-1/2$.
3. Electrons in the same orbital have opposite spins.
4. Electrons with the same spin don’t repel each other as much as electrons with opposite spins do.
5. No two electrons in the same atom can have the same 4 quantum numbers (Pauli’s Exclusion Principle).

Electronic configurations are sometimes represented pictorially, with a box representing an orbital and arrows in the up and down direction representing electrons.

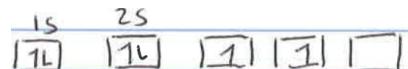


Figure 11: Carbon ground state electron configuration.

1.13 Radial Distribution Functions

We can illustrate nodes through a **radial distribution function**.

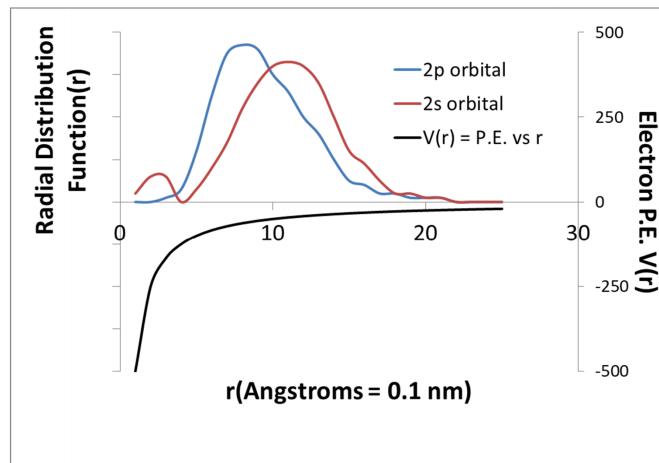


Figure 12: Radial distribution function.

All s orbitals ($l = 0$) have non-zero values of Ψ , so no nodes, at the nucleus. All orbitals with $l \geq 1$ have nodes through the nucleus. This is because l is the number of angular nodes, which all go through the nucleus.

If Ψ were the only factor for electron positional probability, then all electrons in s-orbitals would be incredibly close to the nucleus, with the most probable distance being 0. However, this is not the case, since the **radial distribution function**, $4r^2(\Psi(r))^2$, grows exponentially as r increases - therefore, the radial probability looks more like a parabola, with the most probable distance being further from the nucleus. In essence, because the number of positions r -distance away from the nucleus increases, the probability of being r -distance away from the nucleus increases as well.

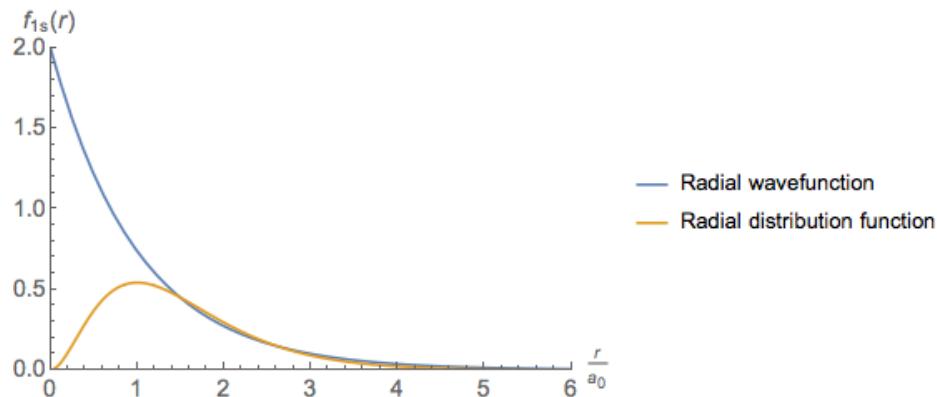


Figure 13: Radial Distribution vs Radial Wave Function

The above is a radial distribution curve - notice how the most probable distance is not the same as the maximum of the wave function.

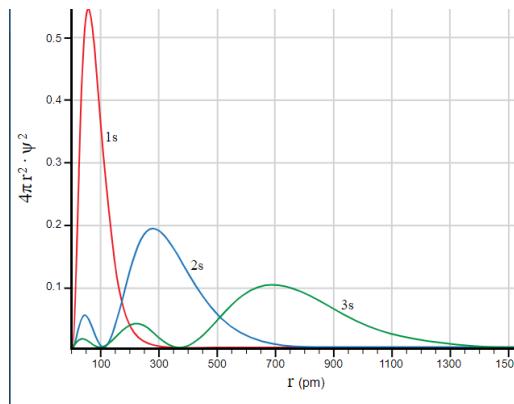


Figure 14: 1s vs 2s vs 3d

The above is a comparison between n -values for an s-orbital. Notice how radial nodes are represented.

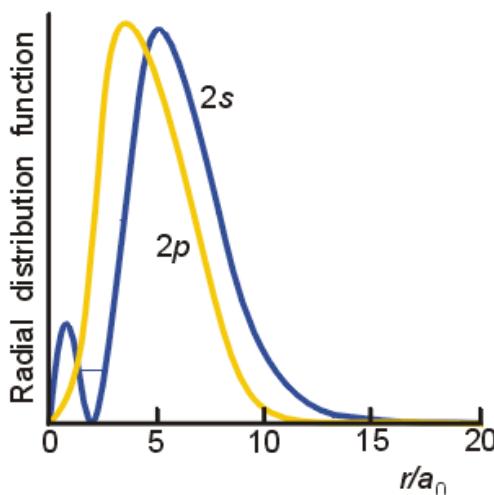


Figure 15: 2s vs 2p

The above is a comparison between the 2s and the 2p atomic orbitals. Notice how the 2p orbital has no radial node, but the 2s orbital does. Notice also that the small initial 2s peak contributes to **penetration**, which is what allows the 2s orbital to remain lower in energy than the 2p orbital. Because the 2s orbital has a higher probability close to the nucleus than the 2p orbital, electrons are able to be there.

1.14 Periodic Trends

Elements in the same periodic table column have similar valence electron configurations, which produce similar reactivities.

Atomic Radius

- Decreases along a row since as nuclear charge grows, electrons are pulled tighter.
- Increases down a column since increasing n of valence electron increases distance of electrons.
- Large jump in radius from the end of a row to the start of the next.

Ionization Energy

- Increases along a row as Z_{eff} grows, so electrons are closer to the nucleus.
- Decreases along a column as n grows, so electrons are further away from the nucleus.

Electronegativity

- Increases along a row as Z_{eff} grows, so electrons are pulled closer to the nucleus.
- Decreases along a column as n grows, so electrons are pulled less closely to the nucleus.

1.15 Ionization Energy

Ionization energy is the minimum energy required to remove the highest energy electron in an atom or ion. For hydrogen and other single electron atoms and ions, calculating ionization energy is as simple as using Rydberg's equation. However, this equation can also be applied to multi-electron atoms, albeit indirectly.

Atom	e^-	Z	e^- Config	n	Rydberg	Measured
H	1	1	$1s^1$	1	13.6eV	13.6ev
He	2	2	$1s^2$	1	54.4eV	24.6eV
He^+	1	2	$1s^1$	1	54.4eV	54.4eV

As we can see, Rydberg predictions were accurate for atoms and ions with one electron. However, when multiple electrons are present, electron-electron repulsions change the ionization energy value. Another way of thinking about this is that electron-electron repulsions and screening *lower effective nuclear charge*.

As we can see, effective nuclear charge is lower than actual nuclear charge. However, this Z_{eff} value is made-up - it is merely a model that helps us understand the magnitude of electron repulsions and screening. Let's explore lithium as an example:

Atom	# of e^-	Z	e^- Config	n	Rydberg	Measured	Z_{eff}
Li	3	3	$1s^2 2s^1$	2	30.6eV	5.6eV	1.26
Li^+	2	3	$1s^2$	1	122.4eV	75.6eV	2.36
Li^{2+}	1	3	$1s^1$	1	122.4eV	122.4eV	3

We see similar results to what we saw above. Notice that the Li atom had a much lower predicted and measured value than the other two. This is because electrons closer to the nucleus screen electrons further from the nucleus more effectively. Electrons weakly screen electrons at similar distances.

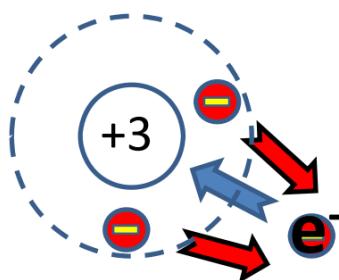


Figure 16: Inner electrons screen outer electron interaction with the nucleus.

Notable Exceptions

Two notable exceptions to the ionization energy trend arise quite readily. They are largely due to the ways that electrons are allocated according to Hund's rule. In short, when removing an electron leads to half-filled or empty shells, the process is slightly more favourable, leading to a lower ionization energy.

1. The first ionization energy of Boron is less than that of Beryllium.
2. The first ionization energy of Oxygen is less than that of Nitrogen.

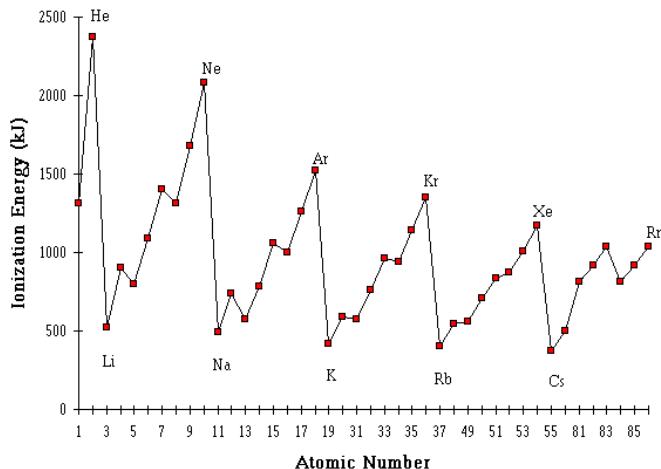


Figure 17: Ionization energy trends.

1.16 Hund's Rule

Hund's rule states that electrons will populate degenerate (same energy) orbitals with electrons of the same spin before double-populating any degenerate orbitals. We can see this in the diagram below. This is because electrons with opposite spin generate more repulsion than those with the same spin, and because putting two electrons in the same orbital generates repulsion as well. Hund's rule is incredibly impactful for elements with partially filled *d* and *f* orbitals.

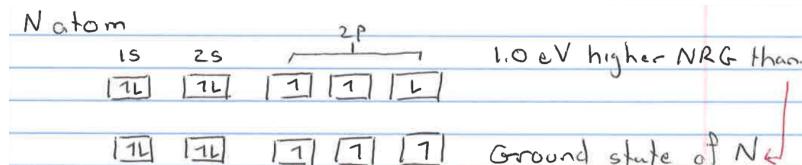


Figure 18: Hund's rule in nitrogen.

Spin Physics

Two electrons with opposite spins can get close to one another (generating repulsion). However, two electrons with the same spin cannot populate the same space. Therefore, two electrons in different orbitals with the same spin generate less repulsion, since they stay away from one another.

Notable Exceptions

Chromium (Cr) has an atomic electron configuration of $4s^13d^5$ instead of the expected $4s^23d^4$. As well, Copper (Cu) has an atomic electronic configuration of $4s^13d^{10}$ instead of the expected $4s^23d^9$. This is because there is less electron-electron repulsion generated from having 6 electrons share the same spin. In easy-to-remember terms, atoms like having half-filled shells and full-filled shells, and will give up one electron in an s-orbital to attain it. Note that this trend carries on for elements with similar atomic electron structures, and that this explains deviations in ionization energy which we won't discuss (think, a half- or full-filled shell is stable!).

Atom	Z	Electron Configuration: $3d$									
		4s									
Potassium (K)	19	$[Ar]4s^1$	1	□	□	□	□	□	□	□	
Calcium (Ca)	20	$[Ar]4s^2$	11								
Scandium (Sc)	21	$[Ar]4s^23d^1$	11	1	□	□	□	□	□	□	
Titanium (Ti)	22	$[Ar]4s^23d^2$	11	1	1	1	1	1	1	1	same m_s !
Vanadium (V)	23	$[Ar]4s^23d^3$	11	1	1	1	1	1	1	1	" "
Chromium (Cr)	24	$[Ar]4s^13d^5$	11	1	1	1	1	1	1	1	
Manganese (Mn)	25	$[Ar]4s^23d^5$	11	1	1	1	1	1	1	1	all 6 spins parallel!!
Iron (Fe)	26	$[Ar]4s^23d^6$	11	1	1	1	1	1	1	1	
Cobalt (Co)	27	$[Ar]4s^23d^7$	11	1	1	1	1	1	1	1	
Nickel (Ni)	28	$[Ar]4s^23d^8$	11	1	1	1	1	1	1	1	
Copper (Cu)	29	$[Ar]4s^13d^9$	11	1	1	1	1	1	1	1	
Zinc (Zn)	30	$[Ar]4s^23d^{10}$	11	1	1	1	1	1	1	1	

Figure 19: Hund's Rule for Transition Metals.

1.17 Electron Affinity

Electron affinity is the energy released when an atom gains an electron. If electron affinity is negative, the atom will accept an electron, and the process is exothermic. If a purported electron affinity is positive, the atom will not accept the electron, and there is actually no electron affinity. Electron affinity gets more negative along a row (since higher $Z_{eff} \rightarrow$ tighter hold on new electrons) and more positive along a column (since larger atoms will hold new electrons less tightly). Note that we can use electron affinity values to calculate Z_{eff} .



2 Atomic Structure

2.1 Bonding

Bonds are formed through reactions. Bonding lowers energy by allowing electrons to be attracted to two nuclei in a larger bonding orbital. The characteristic of **bond formation** is that (1) the reactions release energy upon formation, and (2) the nuclei maintain (nearly) constant separation in the product. The change in energy is known as the **bond energy**, and the distance between nuclei is known as the **bond length**. Note that a higher bond energy corresponds to a stronger bond, and a shorter bond length.

In the context of **Lewis structures**, bonding is a way that atoms can share electrons between themselves equally, stabilizing both. Bonding can be characterized with a drop in potential energy for both the atoms involved. There are a few different kinds of bonds:

- **Non-polar Covalent:** A bond formed between atoms which shares the electrons equally. The atoms should have relatively similar electronegativities (within 0.5). Often between nonmetals.
- **Polar Covalent:** A bond in which the electrons are polarized, or held closer, toward the atom with the higher electronegativity. Occurs when the difference is greater than 0.5 but less than 2. Often between nonmetals.
- **Ionic:** A bond where the electrons are heavily favored toward the atom with the higher electronegativity, occurring when the difference in electronegativity is more than 2.5. Occurs between a nonmetal and a metal, where the metal donates its electrons to the nonmetal and forms ions.
- **Metal:** A ‘sea of electrons’ that occurs in metals.

2.2 Lewis Structures

Lewis Structures are a model for representing atomic bonds and lone pairs. Each bond in a Lewis Structure is shared equally, each atom getting 2 electrons per bond.

In order for a structure to be considered ‘stable’, we follow what is called the **octet rule**. Other than H, which only needs 2 electrons to be stable, most atoms need 8 electrons. Notable exceptions to this rule include Be, which is stable with 4, B and Al, which are stable with 6 (plus a coordinate covalent bond), and 3rd period elements, which can expand their octets beyond the 8 electrons.

Common patterns:

- **F, Cl, Br, I (ns^2np^5)**: Form 1 covalent bond
- **O, S, Se (ns^2np^4)**: Form 2 covalent bonds
- **N, P, As (ns^2np^3)**: Form 3 covalent bonds
- **C, Si, Ge (ns^2np^2)**: Form 4 covalent bonds
- **B and Al**: Form 3 bonds plus a coordinated covalent bond

2.3 Formal Charge

Electrons are sometimes shared unequally in bonds. We use **formal charge** to specify atoms with unusually high or low electron densities. When choosing between multiple possible candidates for a molecular structure for a given set of atoms, the structure with the least formal charge is preferred.

$$\boxed{\text{Formal Charge} = (\# \text{ of Valence } e^-) - (\# \text{ of bonds}) - (\# \text{ of lone pair } e^-)} \quad (15)$$

2.4 Resonance

Sometimes there are multiple correct Lewis structure for a given molecule. To show that multiple structures are correct, we use **resonance structures**. In this case, no single structure wholly encapsulates the nature of the bonding and charge distribution between the atoms. We draw multiple Lewis structures and draw double sided arrows between them, enclosing everything in square brackets:

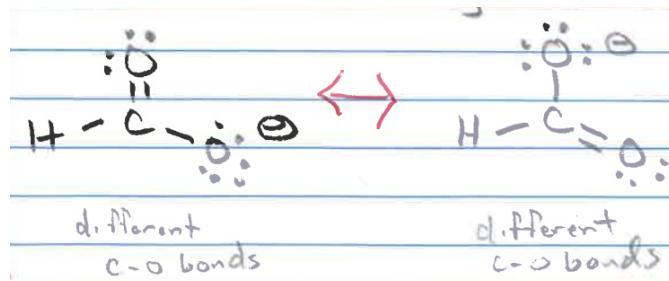


Figure 20: Resonance structures.

Sometimes an overall representation of the molecule can be made that contains parts from all of the resonance structures, called a resonance hybrid.

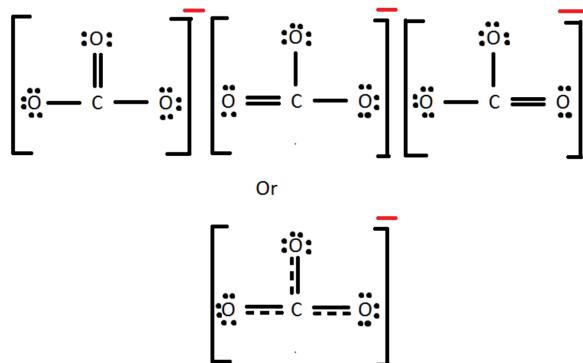


Figure 21: Resonance hybrid.

2.5 VSEPR

Lewis structures are decent for understanding bonding and localized electron density. But if we want to understand the 3D geometry of a molecule, we have to use the **VSEPR** model (Valence Shell Electron Pair Repulsion). The whole idea behind this model is to maximize the distance between electron pairs to minimize repulsion. We can construct a table for the geometries of the occupied spaces (lone pairs and bonds) around a central atom A:

Occupied areas	Geometry
1, 2	Linear
3	Trigonal planar
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

Note that lone pairs and atoms affect bond angles differently, but this discussion is beyond the scope of this course.

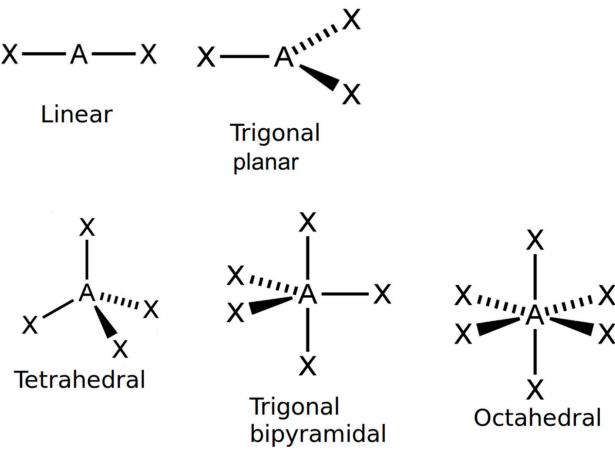


Figure 22: 3D VSEPR Structures.

2.6 Electronegativity

Electronegativity is defined as a bonded atom's ability to shift shared bonding electrons towards itself. We can look up electronegativity values on a table: the higher the value, the stronger the atom's hold on electrons. If the

bond electronegativity difference is 0, then the bond is non-polar. If it is between 0.1 and 0.5, it is weakly polar. If it is between 0.5 and 2, is polar. If it is above 2.5, it is likely ionic.

A polar bond has a **bond dipole**, and the **dipole moment** of a molecule is the vector sum of its bond dipoles. This is how we determine whether entire molecules are polar or not - if a molecule has a net dipole moment, it is polar; otherwise, it is nonpolar. Symmetric molecules with polar bonds are nonpolar, since their bond dipoles will sum to zero. Asymmetric molecules with polar bonds are polar, since their bond dipoles do not sum to zero. Any molecule with purely nonpolar bonds is nonpolar, since there are no bond dipoles to sum.

An example of a symmetric molecule with polar bonds is CCl_4 , in which each C-Cl bond is polar, but the molecule's overall perfectly symmetric tetrahedral structure leads to the complete cancellation of the moments.

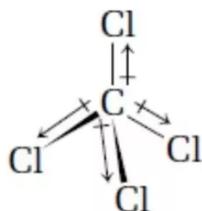


Figure 23: Dipole moment cancellation in CCl_4 .

Nonzero net dipole moments lead to interesting properties, such as stronger intermolecular forces. More polar molecules attract each other more than nonpolar molecules, raising their boiling point noticeably. A special kind of bonding known as hydrogen bonding raises boiling point even more, which is how water is a liquid at room temperature.

2.7 Molecular Orbitals

Omitted here is the explanation of MOs through the lens of PIB. If, for some ungodly reason, this is interesting to you, please review class slides from 10-09.

Considering the case for a homogeneous diatomic molecule (like H_2), combining the wave functions of each individual atom can approximate their molecular orbitals. In the case that we add the wave functions (in phase combination), electron density is concentrated between the nuclei. This configuration lowers potential energy, since electrons are attracted to both nuclei, and nuclei repulsion is shielded by the electrons. Any configuration that lowers energy is called a **bonding molecular orbital**.

In the case that we subtract the wave functions (out of phase combination), electron density is not concentrated between the nuclei. This configuration increases potential energy, since nuclei-nuclei repulsion isn't shielded, and no new electron attractions were formed. Moreover, a node is formed, increasing energy. Any configuration that increases energy is called an **antibonding molecular orbital**. All of these observations can be re-framed through the PIB model and “waviness”.

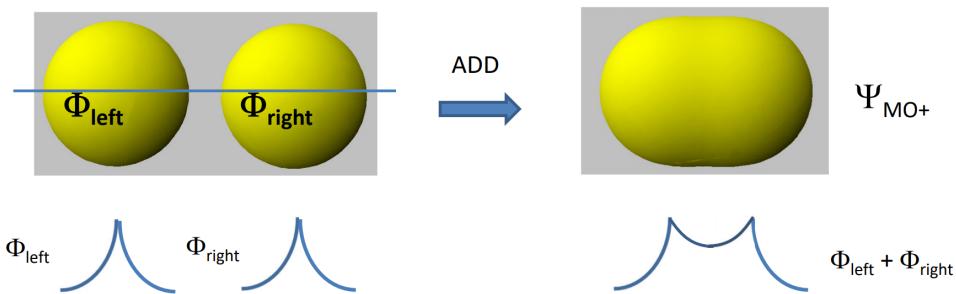


Figure 24: Wave function for bonding MOs.

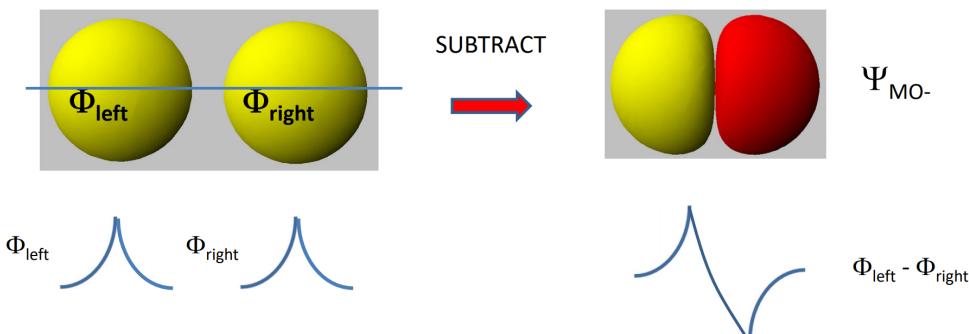


Figure 25: Wave function for antibonding MOs.

We can sum up the mathematical approximations as follows:

$$\boxed{\Psi_{\text{MO+}} \approx \Phi_{\text{Left}} + \Phi_{\text{Right}}} \quad (16)$$

$$\boxed{\Psi_{\text{MO-}} \approx \Phi_{\text{Left}} - \Phi_{\text{Right}}} \quad (17)$$

σ -bonds are formed from s-orbitals or p-orbitals that lie along the internuclear axis, and π -bonds are formed from p-orbitals that lie perpendicular to the internuclear axis. To determine if an MO is a σ -bond MO visually, look down the inter-nuclear axis: a σ -bond is cylindrically symmetric. To determine if an MO is a bonding MO or an anti-bonding MO, compare the number of nodes.

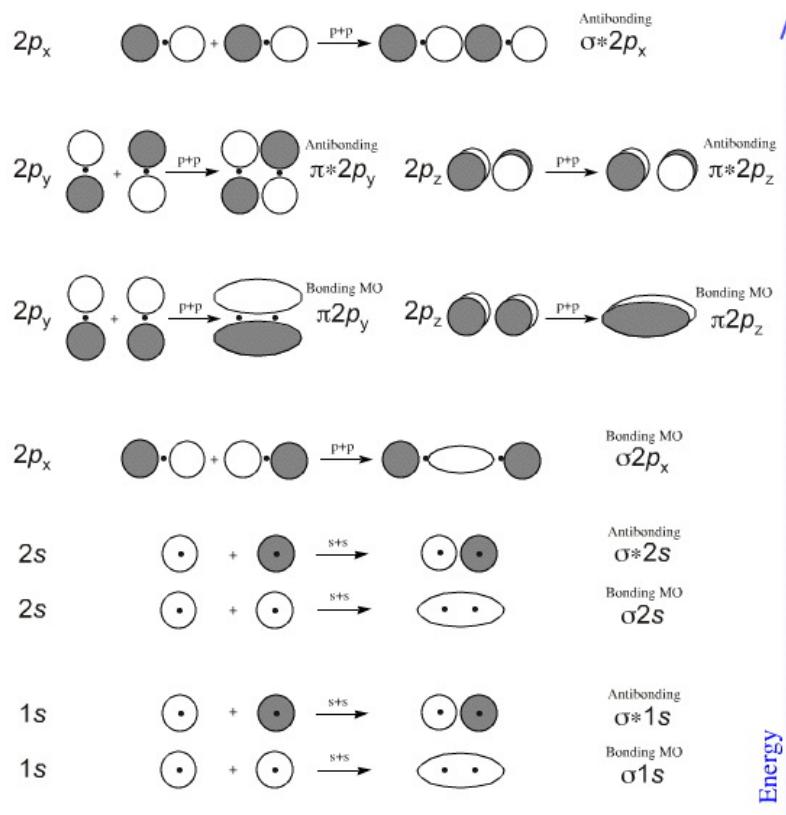


Figure 26: A number of molecular orbitals.

2.8 MO Energy Diagrams

We can visualize the energies of different MOs through an energy diagram.

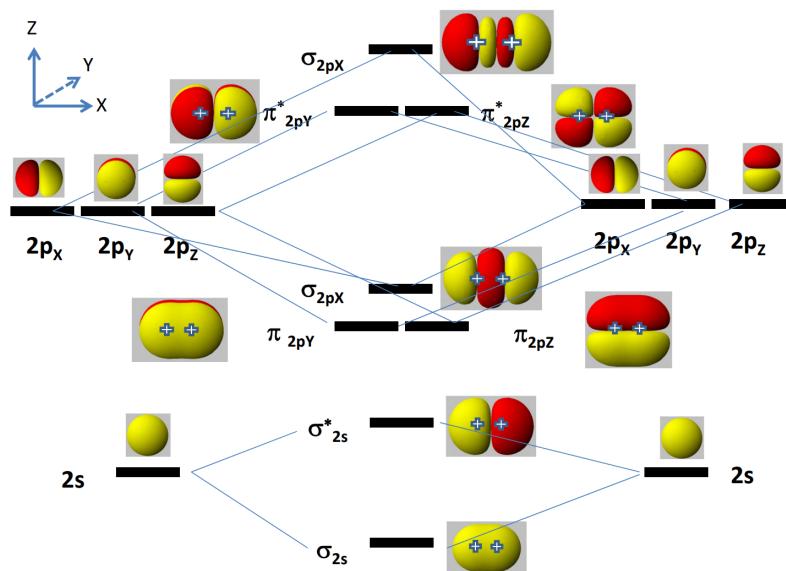


Figure 27: MO energy diagram for s and p orbitals..

Paramagnetism and Diamagnetism

This is best explained by a picture. Essentially, **paramagnetic** atoms have unpaired electrons in the MO energy diagram, while **diamagnetic** atoms have all electrons paired in the MO energy diagram.

	Diamagnetic	Paramagnetic
Electron pairing	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow$ No unpaired electrons	$\uparrow\downarrow \uparrow\downarrow \uparrow$ At least one unpaired electron

Figure 28: Diamagnetic vs. Paramagnetic.

2.9 Bond Order

Bond order is the number of bonds a molecular orbital has. A bond order ≤ 0 implies that the bond does not form. The higher the bond order, the stronger and shorter the bond.

$$\text{Bond Order} = \frac{\# \text{ e}^- \text{ bonding MO} - \# \text{ e}^- \text{ antibonding MO}}{2} \quad (18)$$

2.10 MOs of Heteronuclear Diatomics

In homogeneous diatomics, electrons are shared equally, meaning each atom got around 50% of the electron density near them. Heteronuclear diatomics, which are molecules with two distinct elements, are unique in that they have a dipole moment, so electrons are not shared equally. Therefore, both MO shapes and MO energy diagrams are different.

The more electronegative atom will be lower in energy, and will hold a larger proportion of electron density. This skews MO energy diagrams, making the more electronegative atom's lower on the diagram, and affects MO shapes by bloating the more electronegative side on a bonding MO and bloating the less electronegative side on an anti-bonding MO. A good way to remember this last property is to know that each atom will have the larger percentage of electron density from the MO that is closest in energy to it - more electronegative to bonding, less electronegative to anti-bonding.

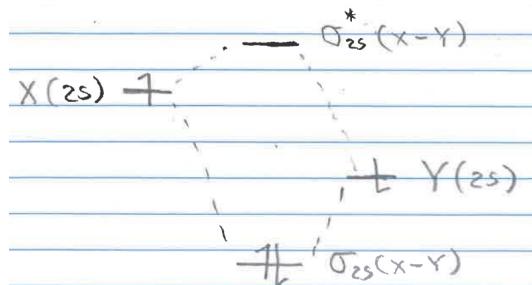


Figure 29: MO for heterogenous molecule.



Figure 30: MO heterogenous: bonding.



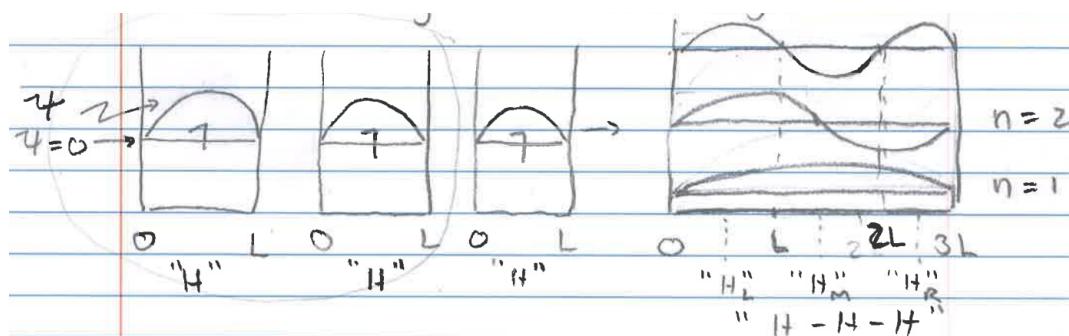
Figure 31: MO heterogenous: antibonding.

2.11 MOs of Triatomics

As a case study, take the hypothetical compound H_3 and compare it to the known H_2 . We know that the H_2 σ -bond delocalizes electrons over two nuclei, lower energy. If our H_3 wave functions were combined in-phase (MO #1), there would be no nodes and electrons would be delocalized over three nuclei, thus: $E_{\text{MO}\#1} < E_{1s}(\text{H})$ and $E_{\text{MO}\#1} < E_{\sigma}(\text{H}_2)$.

Now, take the case where we combine the wave functions of H_3 out of phase (MO #3). In this case, there are two nodes, and energy would increase. Therefore: $E_{\text{MO}\#3} > E_{1s}(\text{H})$ and $E_{\text{MO}\#3} > E_{\sigma^*}(\text{H}_2)$

However, there leaves the case where there is only one node - in this case, the node is on the central H nucleus, where $\Psi = 0$. This molecular bonding orbital (MO #2) is known as a **non-bonding molecular orbital**, since it neither raises nor lowers energy of the atoms. $E_{\text{MO}\#2} = E_{1s}(\text{H})$

Figure 32: Energy levels of H_3 MOs.

An important question is why we don't observe H_3 in nature if it is lower in energy than H_2 . The short answer can be modelled through an example: in a system with 6 H ions, forming 3 H_2 molecules produces 6 bonding electrons, while forming 2 H_3 molecules produces 4 bonding electrons and 2 non-bonding electrons, which we can see from filling the diagram above. In real systems, H is abundant, so the former case will always be preferred. However, H_3^+ can form in a cyclic manner, because each H nucleus has two bonding overlaps, making it rather stable.

2.12 Hybridization

Hybridization helps us better understand the shape around atoms with relation to atomic orbitals. By combining wave functions of atomic orbitals, we can generate **hybridized orbitals** which better explain the shape of bonded atoms. Each bonding nuclei can become hybridized in a few main ways, and each one corresponds to a VSEPR shape:

- sp - linear
- sp^2 - trigonal planar
- sp^3 - tetrahedral
- sp^3d - trigonal bipyramidal
- sp^3d^2 - trigonal planar

Hybridization works by combining atomic orbitals, and we will always get as many hybridized orbitals as we put in atomic orbitals. A good way to know how bonding nuclei are hybridized is to remember that the number of bonding neighbors is equal to the number of atomic orbitals inputted, and therefore equal to the number of hybridized orbitals.

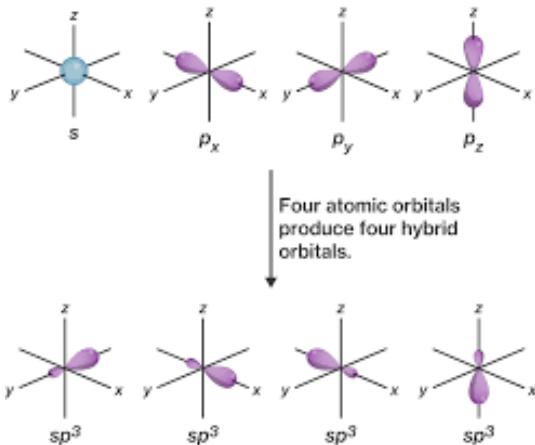


Figure 33: sp^3 hybridization.

3 Thermodynamics

3.1 Energy

We have already talked about energy a bit, but it is useful to define some more terms before we proceed:

- **Heat:** Energy transferred due to a temperature difference.
- **Work:** Energy transferred due to applying a force over a distance.

Note that energy is a **state function**, meaning its value does not depend on the path a process takes. Rather, all that matters is its current state. Heat and work, on the other hand, are both **path functions**. One cannot find the heat or work for a process if no pathway is specified (either explicitly or implicitly).

State functions other than Internal Energy (U) include Pressure (P), Volume (V), Temperature (T), Enthalpy (H), Entropy (S), Free Energy (G), and more. As they are not path dependent, we can use state functions to characterize a system.

3.2 Temperature and Kinetic Energy

Using the **ideal gas law** and a simplified model of an ideal gas particle in a cubic box, we can derive a relationship between the temperature and average translational kinetic energy of a gas. For a mole of ideal gas particles, we have:

$$KE = \left(\frac{1}{N_A} \right) \frac{3}{2} RT \quad (19)$$

where N_A is Avogadro's number.

Knowing that $KE = \frac{1}{2}mv^2$ then allows us to rearrange this relationship in order to find the **root mean square velocity** of the gas particles:

$$u_{rms} = \sqrt{\frac{3RT}{M}} \quad (20)$$

Where M is molar mass. It is important to note that since this is a root mean square velocity, there are many gas particles moving faster and slower than this average.

3.3 The First Law of Thermodynamics

The **First Law of Thermodynamics** states that the total energy (U or E) of the universe is constant. If we divide the universe into the **system** and the **surroundings**, we can say:

$$U_{universe} = U_{sys} + U_{surr} \quad \& \quad \Delta U_{universe} = \Delta U_{sys} + \Delta U_{surr} = 0 \quad (21)$$

Furthermore, when we consider the different ways we can change the internal energy of a system, we have:

$$\Delta U = U_f - U_i = q + w \quad (22)$$

where q is the heat *added to* the system and w is the work *done on* the system (sign conventions are important to know). Also, one should note that even though q and w are both path functions, their sum, U , is a state function.

Heat

The flow of heat between a system and its surroundings can characterize processes as either **endothermic** or **exothermic**. In the endothermic case, $q > 0$ and heat flows *into* our system from the surroundings, increasing the system's internal energy U_{sys} . On the other hand, in the exothermic case, $q < 0$, implying that heat flows *out of* the system and into the surroundings, decreasing U_{sys} . When $q = 0$, the process is **adiabatic** and has some interesting properties that can be explored later.

Work

We use w to denote the work done *on* the system, meaning that a positive w means the surroundings do work on the system. This is consistent with our equation for the change in internal energy, where we have $w > 0 \implies \Delta U > 0$. If $w < 0$, then our system is doing work on the surroundings and thus using up some of its internal energy, so $w < 0 \implies \Delta U < 0$. As work is described generally by force applied over distance, for the expansion of a gas, we get:

$$w = - \int P_{ext} dV = -P_{ext} \Delta V \quad (23)$$

simplifying in the case where P_{ext} is a constant (note $1 \text{ atm} \cdot 1 \text{ L} = 101.3 \text{ J}$). Since P_{ext} is always non-negative, a negative ΔV corresponds to a positive w , which means the surroundings did work on the system to compress it. Vice versa, a positive ΔV corresponds to a negative w , meaning that the system needed to do work on the surroundings in order to expand. We can see that if $\Delta V = 0$ or $P_{ext} = 0$, then $w = 0$. This means that constant volume processes involve no work, along with implying that expansion at an external pressure of 0 takes no work. Expanding into a vacuum where $P_{ext} = 0$ is called a **free expansion** and will be discussed later.

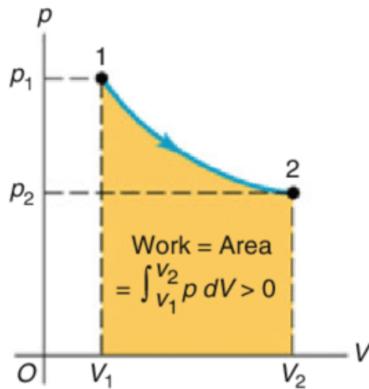


Figure 34: Integral of the PV process.

For a *constant volume* process:

$$\boxed{\Delta V = 0 \implies w = 0 \implies \Delta U = q} \quad (24)$$

If the volume stays constant then no work is done and thus the internal energy would only be changed with heat flow. This motivates the idea that for any gas:

$$\boxed{\Delta U = nC_V\Delta T} \quad (25)$$

where C_V is called the **constant volume molar heat capacity**. Our previous expression for KE implies that for an ideal monoatomic gas, $C_V = \frac{3}{2}R$. Thus we see that the internal energy change for a process only depends on the gas's temperature change, no matter if the volume was actually kept constant.

3.4 Enthalpy

We define a new state function, Enthalpy (H) as:

$$\boxed{H = U + PV \implies \Delta H = q + V\Delta P} \quad (26)$$

For a *constant pressure* process we find that:

$$\boxed{\Delta P = 0 \implies \Delta H = q} \quad (27)$$

Similar to the internal energy, the change in enthalpy is only dependent on the change in temperature (even for non-constant pressure processes):

$$\boxed{\Delta H = nC_P\Delta T} \quad (28)$$

where C_P is called the **constant pressure molar heat capacity**. Heating a gas at constant pressure:

$$\Delta H = nC_P\Delta T = q = \Delta U + P\Delta V = nC_V\Delta T + nR\Delta T = n(C_V + R)\Delta T \implies$$

$$\boxed{C_P = C_V + R} \quad (29)$$

3.5 Isothermic Processes

An **isotherm** is a pressure-volume curve on which T is constant. Between two states I and F on this isotherm, we know that:

$$\boxed{\Delta T = 0 \implies \Delta U = \Delta H = 0} \quad (30)$$

As U and H are state functions, this 0 sum should be the same no matter the actual process we use to get from I to F . We can choose to either do a constant volume process first and then a constant pressure process, or a constant pressure process first and then a constant volume process. These two paths will have varying q and w values, yet the sums should still remain the same. This same analysis will work the same exact way if I and F are at different temperatures, the only difference being that ΔU and ΔH will not be 0 (instead each will be their own constants that won't vary with the choice of path).

3.6 Standard States

We define **standard states** for different states of matter as:

- **A gas:** A pressure of 1 atm.
- **A liquid/solid:** The pure substance.
- **In solution:** A concentration of 1.0 M at 1 atm.

The lowest energy form of a pure element at 1 atm and 298 K has:

$$\boxed{\Delta H_{f, 298}^\circ = 0} \quad (31)$$

The **standard enthalpy of formation** is defined as the heat released (at constant pressure) when one mole of the product is formed from its constituent elements in their standard states. With this idea of standard enthalpies of formation, we arrive at **Hess's Law**, which allows us to algebraically manipulate reactions into a desired target, combining ΔH values as we go along:

$$\boxed{\Delta H_{rxn, T}^\circ = \sum_{\text{products}} \Delta H_{f, T}^\circ - \sum_{\text{reactants}} \Delta H_{f, T}^\circ} \quad (32)$$

3.7 The Second Law of Thermodynamics

The **Second Law of Thermodynamics** says that in order for a process to be spontaneous:

$$\boxed{\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} > 0} \quad (33)$$

As our universe proceeds in a spontaneous manner, the entropy of the universe is always increasing.

3.8 Entropy

Entropy (S) is a very important state function that governs the spontaneity of processes. An increase in entropy is associated with increasing probability, which can be seen through **microstates**. In our case, a microstate is a possible arrangement of the gas particles in the system. The state with the most number of microstates is thus the most probable, and said to have the highest entropy.

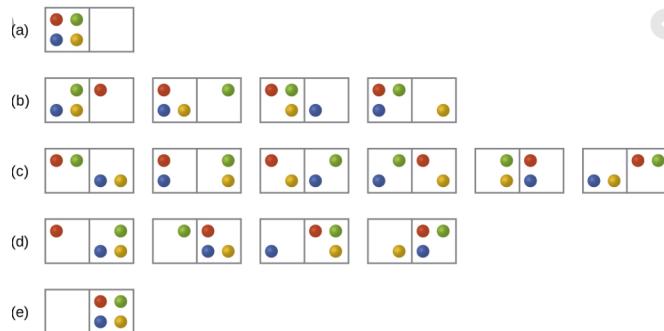


Figure 35: Different microstates.

Boltzmann defined entropy as:

$$S = k_B \ln \Omega \quad (34)$$

where k_B is Boltzmann's constant and Ω is the number of microstates. With this definition, we find that the change in entropy for an adiabatic free expansion at constant temperature is:

$$\Delta S = nR \ln \frac{V_f}{V_i} \quad (35)$$

We can see that even for a constant temperature (and thus constant energy & enthalpy) process, as long as $V_f > V_i$, the entropy will increase and thus the process is spontaneous. This makes sense intuitively since gas will tend to expand into larger volumes whenever possible.

3.9 Temperature and Entropy

We just saw how increasing the volume of a gas increases its entropy by increasing its number of available **position related microstates**. But, we can also increase the entropy of a gas by increasing its temperature, which increases its number of available **velocity related microstates**. We get that for a *constant volume* process:

$$\Delta V = 0 \implies dU = nC_V dT = dq \implies \Delta S = \int \frac{dq}{T} = \int \frac{nC_V dT}{T} = nC_V \ln \frac{T_f}{T_i} \quad (36)$$

And for a *constant pressure* process:

$$\Delta P = 0 \implies dH = nC_P dT = dq \implies \Delta S = \int \frac{dq}{T} = \int \frac{nC_P dT}{T} = nC_P \ln \frac{T_f}{T_i} \quad (37)$$

3.10 Reversible and Irreversible Processes

A **reversible** process is a process which can be ‘reversed’ by changing one of the properties infinitesimally. We can use this theoretical process to explore the maximum work an expanding gas can perform on its surroundings. If we match the internal pressure of the gas equally with an external force as it expands, we maximize the work done and maximize the amount of heat flow into the system. For a reversible and isothermal process:

$$w_{rev} = - \int P_{ext} dV = - \int \frac{nRT}{V} dV = -nRT \ln \frac{V_f}{V_i} \quad (38)$$

Since in an isothermal expansion $\Delta T = 0 \implies \Delta U = 0 \implies q = -w$:

$$q_{rev} = -w_{rev} = nRT \ln \frac{V_f}{V_i} \quad (39)$$

This expression for the reversible heat looks familiar:

$$\Delta S_{sys} = \left(\frac{1}{T} \cdot T \right) \cdot nR \ln \frac{V_f}{V_i} = \frac{q_{rev}}{T} \quad (40)$$

We derived this from the reversible case but as ΔS_{sys} is a state function, this holds regardless of whether our process is reversible or irreversible. For any constant temperature process this formula is valid. Even though q is normally a path function, q_{rev} will be unique since the pathway is implicitly specified. Note that the surroundings will always deliver and absorb heat reversibly.

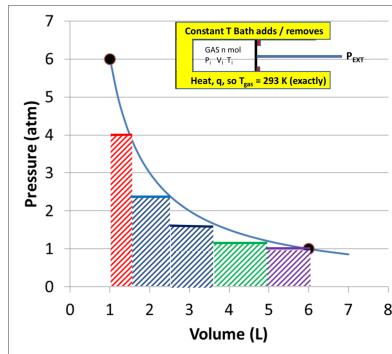


Figure 36: Isotherm integral.

3.11 Spontaneity

In order to determine if a given process is spontaneous (or *irreversible*), we only must consider the sign of $\Delta S_{universe}$. If and only if this change is greater than zero, we know that the process is spontaneous.

3.12 Phase Transitions

Let’s look at an example of a phase transition from a solid to a liquid. Note that phase transitions at the transition temperature are reversible processes ($\Delta S_{universe} = 0$). So for the entropy change of the system at a constant pressure:

$$\Delta S_{transition} = \frac{q_{rev}}{T_{trans}} = \frac{n \Delta H_{transition}}{T_{trans}} \quad (41)$$

where $\Delta H_{transition}$ is measured per mole. Taking this a step further we see:

$$\boxed{\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{transition} - \frac{n \Delta H_{transition}}{T_{curr}}} \quad (42)$$

Since we have our equation for $\Delta S_{transition}$, we see that for an endothermic process where $\Delta H > 0$, the transition will be spontaneous if and only if $T_{curr} > T_{trans}$ (from the difference of their reciprocals). This condition is reversed for an exothermic process.

When talking about phase transitions, we should know that:

$$\boxed{S_{solid} < S_{liquid} < S_{gas}} \quad (43)$$

Also, to calculate the entropy change of a substance that undergoes both phase transitions and temperature changes, one must simply add the entropy of each step together (where the entropy varies logarithmically within a phase). Note that the **Third Law of Thermodynamics** states that the entropy of a pure crystal (of any element) is 0 at 0 K.

3.13 Gibbs Free Energy

We define a new state function, **Gibbs free energy** (G) as (at constant temperature and pressure):

$$\boxed{G = H - TS \implies \Delta G = \Delta H - T\Delta S} \quad (44)$$

Taking a look at $\Delta S_{universe}$:

$$\begin{aligned} \Delta S_{universe} &= \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T} = \Delta S_{sys} - \frac{\Delta H}{T} \implies \\ &\quad -T\Delta S_{universe} = \Delta H - T\Delta S = \Delta G \end{aligned} \quad (45)$$

Here we see that we can find the sign of $\Delta S_{universe}$ by only considering aspects of the system. We also see that:

- $\Delta G < 0$: $\Delta S_{universe} > 0$ so the process is spontaneous.
- $\Delta G > 0$: $\Delta S_{universe} < 0$ so the process is not spontaneous.
- $\Delta G = 0$: $\Delta S_{universe} = 0$ so the process is reversible.

Looking at ΔG for the different cases of ΔH and ΔS :

	$\Delta H > 0$	$\Delta H < 0$
$\Delta S > 0$	Spontaneous at $T = \infty$	Always spontaneous
$\Delta S < 0$	Never spontaneous	Spontaneous at $T = 0$

Similar to the standard enthalpy of formation, we have a notion for the **standard free energy of formation** that is defined exactly the same way, substituting the enthalpies for free energies. Again we say that the lowest energy form of a pure element at 1 atm and 298 K is:

$$\boxed{\Delta G_{f, 298}^\circ = 0} \quad (46)$$

When we vary beyond the standard state with a different pressure than 1 atm (but at constant temperature):

$$\Delta G_{f, P_x} = \Delta G_{f, T}^\circ + \Delta H - T\Delta S = \Delta G_{f, T}^\circ + RT \ln P_x \quad (47)$$

Note that this is only for a gas (or a solution), as the chemical potentials of liquids and solids do not vary with pressure.

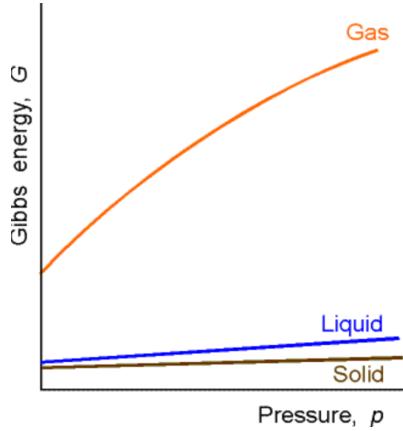


Figure 37: Free Energy (G) vs. Pressure (P)

Considering the vaporization of a liquid to a gas at a constant external pressure of P_{ext} :

$$\Delta G = 0 = \Delta G_{rxn}^\circ + RT \ln P_{ext} = \Delta H^\circ - T_{BP} \Delta S^\circ + RT_{BP} \ln P_{ext} \implies T_{BP} = \frac{\Delta H^\circ}{\Delta S^\circ - R \ln P_{ext}} \quad (48)$$

With our chemical potential formula we get that for a general reaction:

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (49)$$

where Q is the reaction quotient.

4 Equilibrium

4.1 K_{eq} and Gibbs Free Energy

When the reaction has reached equilibrium, we know that $\Delta G = 0$ (since it is the ‘driving force’):

$$\Delta G = 0 \implies \Delta G^\circ = -RT \ln K_{eq} \quad (50)$$

where K_{eq} is called the **equilibrium constant** (at equilibrium, $Q = K_{eq}$). For the solubility of salts, we call this special equilibrium constant K_{sp} .

4.2 Temperature Dependence of K_{eq}

At equilibrium, $Q = K_{eq}$. Doing some rearranging we get the **van't Hoff equation**:

$$\Delta G^\circ = \Delta H^\circ - T^\circ \Delta S = -RT \ln K_{eq} \implies$$

$$\boxed{\ln K_{eq} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}} \quad (51)$$

We can also derive a form of the **Clausius Clapeyron equation**:

$$\ln K_1 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} \right) + \frac{\Delta S^\circ}{R} \quad \& \quad \ln K_2 = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} \right) + \frac{\Delta S^\circ}{R} \implies$$

$$\boxed{\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (52)$$

If we apply this to the vaporization of a liquid and use vapor pressures, we see:

$$\boxed{\ln \frac{P_1}{P_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (53)$$

4.3 Le Chatelier's Principle

Le Chatelier's Principle states that if a system at equilibrium experiences a change to perturb the equilibrium, then reactions will occur to attempt to 'offset' the change and return to equilibrium. Increases in concentrations and pressures may change Q , which thus causes reactions to occur to return to K_{eq} .

As seen from the Clausius Clapeyron equation, we have:

- If $\Delta H^\circ > 0$: K_{eq} increases with increasing T .
- If $\Delta H^\circ < 0$: K_{eq} decreases with increasing T .
- If $\Delta H^\circ = 0$: K_{eq} does not change with any variance in T (ΔG° may change but K_{eq} won't).

This can be used to partially explain Le Chatelier's Principle as follows: At equilibrium, $Q = K_{eq}$. If we $\Delta H^\circ > 0$ and we raise the temperature, Q stays the same while K_{eq} increases. $Q < K_{eq}$ means that the reaction will shift towards products, taking in heat (endothermic reaction) and partially offsetting the increase in temperature. The same analysis can be done with an exothermic reaction.

Le Chatelier's Principle also works to offset changes in pressure or volume. A multiplicative increase in all the partial pressures will shift the reaction towards the side with less moles of gas, and vice versa a decrease will shift the reaction towards the side with more moles. If the number of moles are equal, then the reaction will not shift based on multiplicative pressure changes.

The addition of an inert gas to a constant volume vessel does not change any partial pressures and therefore will not cause more reactions to occur.

4.4 Acids and Bases

For the general dissociation of an acid HA into H^+ and A^- , our K_{eq} is called the K_a , or the **acid dissociation constant**:

$$\boxed{K_a = \frac{[H]^+[A]^-}{[HA]}} \quad (54)$$

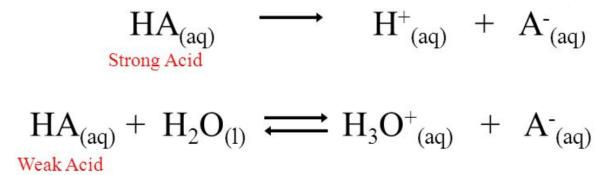


Figure 38: Acid dissociation reaction.

If we consider water to be an acid, we define K_w , the **ion product for water**, as:

$$\boxed{K_w = [\text{H}]^+[\text{OH}]^-} \quad \& \quad \boxed{K_w, 298 \text{ K} = 1.00 \times 10^{-14}} \quad (55)$$

Using an ICE (Initial, Change, Equilibrium) chart, we can solve acid/base equilibrium problems. When using the charts, we often use approximations to simplify the equations (such as approximating away the auto-ionized $[\text{H}]^+ = 1.0 \times 10^{-7} \text{ M}$, or that strong acids dissociate almost completely).

4.5 Henderson-Hasselbalch

We define the pK_a , a modified form of the K_a , as:

$$\boxed{pK_a = -\log_{10} K_a} \quad (56)$$

A **strong acid** is an acid with a large equilibrium constant, such that $K_a > 1 \implies pK_a < 0$. Also note that for the reaction between an acid and a base (producing the conjugate acid and conjugate base):

$$\boxed{K_{eq} = 10^{pK_a, products - pK_a, reactants}} \quad (57)$$

We similarly define the pH as a modified form of the H^+ concentration:

$$\boxed{pH = -\log_{10} [\text{H}^+]} \quad (58)$$

Now we can derive the **Henderson-Hasselbalch equation**:

$$\begin{aligned} \log K_a &= \log \left(\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \right) \implies \\ \boxed{pH} &= pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \end{aligned} \quad (59)$$

From this we see that:

- If the $pH > pK_a$: $[\text{A}^-] > [\text{HA}]$.
- If the $pH < pK_a$: $[\text{A}^-] < [\text{HA}]$.
- If the $pH = pK_a$: $[\text{A}^-] = [\text{HA}]$.

4.6 Buffers

A **buffer** is a solution which contains approximately equal amounts of a weak acid and its conjugate base. Buffers are used to resist changes in the pH if an acid or base is added. From Henderson-Hasselbach we see that:

$$[A^-] \approx [HA] \implies pH = pK_a \quad (60)$$

Buffers can resist changes to the pH only within 1 pK_a unit within the pH , ie. $0.1 < \frac{[A^-]}{[HA]} < 10$. Outside of these bounds, though, the buffer loses its capacity and the pH will change a lot with the addition of a base or acid.

This is the end of the study guide. Thank you for reading! Please let us know if you found any typos or mistakes. Good luck next week!

5 List of Equations

$$\lambda_{object} = \frac{h}{mv} \quad (1)$$

$$\frac{1}{2}m_e v^2 = \frac{h^2}{2m_e \lambda^2} = KE_e \quad (2)$$

$$E_{photon} = h\nu = \frac{hc}{\lambda} \quad (3)$$

$$KE_{electron} = \frac{1}{2}mv^2 \quad (4)$$

$$E_{photon} = \Phi_{metal} + KE_{electron} \quad (5)$$

$$E_{pib} = KE_{pib} = \frac{h^2}{2m_e \lambda_e^2} = \frac{n^2 h^2}{8m_e L^2} \quad (6)$$

$$\lambda_e = \frac{2L}{n} \quad (7)$$

$$PE_e = k \frac{(-q)(Z)}{r} \quad (8)$$

$$\Psi(x, y, z) \implies \Psi(r, \theta, \phi) \quad (9)$$

$$E_n = -13.59 \text{ eV} \frac{Z^2}{n^2} \quad (10)$$

$$\Psi(r, \theta, \phi) = F(r) G(\theta) H(\phi) \quad (11)$$

$$ns < np < nd < nf \quad (12)$$

$$L = l\bar{h} \quad (13)$$

$$Atom_{(g)} + e^- \rightarrow Anion_{(g)}^- \quad \Delta E = \text{electron affinity} \quad (14)$$

$$\text{Formal Charge} = (\# \text{ of Valence } e^-) - (\# \text{ of bonds}) - (\# \text{ of lone pair } e^-) \quad (15)$$

$$\Psi_{MO+} \approx \Phi_{Left} + \Phi_{Right} \quad (16)$$

$$\Psi_{MO-} \approx \Phi_{Left} - \Phi_{Right} \quad (17)$$

$$\text{Bond Order} = \frac{\# \text{ e}^- \text{ bonding MO} - \# \text{ e}^- \text{ antibonding MO}}{2} \quad (18)$$

$$KE = \left(\frac{1}{N_A} \right) \frac{3}{2} RT \quad (19)$$

$$u_{rms} = \sqrt{\frac{3RT}{M}} \quad (20)$$

$$U_{universe} = U_{sys} + U_{surr} \quad \& \quad \Delta U_{universe} = \Delta U_{sys} + \Delta U_{surr} = 0 \quad (21)$$

$$\Delta U = U_f - U_i = q + w \quad (22)$$

$$w = - \int P_{ext} dV = -P_{ext} \Delta V \quad (23)$$

$$\Delta V = 0 \implies w = 0 \implies \Delta U = q \quad (24)$$

$$\Delta U = nC_V \Delta T \quad (25)$$

$$H = U + PV \implies \Delta H = q + V\Delta P \quad (26)$$

$$\Delta P = 0 \implies \Delta H = q \quad (27)$$

$$\Delta H = nC_P \Delta T \quad (28)$$

$$C_P = C_V + R \quad (29)$$

$$\Delta T = 0 \implies \Delta U = \Delta H = 0 \quad (30)$$

$$\Delta H_{f, 298}^\circ = 0 \quad (31)$$

$$\Delta H_{rxn, T}^\circ = \sum_{\text{products}} \Delta H_{f, T}^\circ - \sum_{\text{reactants}} \Delta H_{f, T}^\circ \quad (32)$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} > 0 \quad (33)$$

$$S = k_B \ln \Omega \quad (34)$$

$$\Delta S = nR \ln \frac{V_f}{V_i} \quad (35)$$

$$\Delta S = \int \frac{dq}{T} = \int \frac{nC_V dT}{T} = nC_V \ln \frac{T_f}{T_i} \quad (36)$$

$$\Delta S = \int \frac{dq}{T} = \int \frac{nC_P dT}{T} = nC_P \ln \frac{T_f}{T_i} \quad (37)$$

$$w_{rev} = - \int P_{ext} dV = - \int \frac{nRT}{V} dV = -nRT \ln \frac{V_f}{V_i} \quad (38)$$

$$q_{rev} = -w_{rev} = nRT \ln \frac{V_f}{V_i} \quad (39)$$

$$\Delta S_{sys} = \left(\frac{1}{T} \cdot T \right) \cdot nR \ln \frac{V_f}{V_i} = \frac{q_{rev}}{T} \quad (40)$$

$$\Delta S_{transition} = \frac{q_{rev}}{T_{trans}} = \frac{n \Delta H_{transition}}{T_{trans}} \quad (41)$$

$$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{transition} - \frac{n \Delta H_{transition}}{T_{curr}} \quad (42)$$

$$S_{solid} < S_{liquid} < S_{gas} \quad (43)$$

$$G = H - TS \implies \Delta G = \Delta H - T\Delta S \quad (44)$$

$$-T\Delta S_{universe} = \Delta H - T\Delta S = \Delta G \quad (45)$$

$$\Delta G_{f, 298}^\circ = 0 \quad (46)$$

$$\Delta G_{f, P_x} = \Delta G_{f, T}^\circ + \Delta H - T\Delta S = \Delta G_{f, T}^\circ + RT \ln P_x \quad (47)$$

$$T_{BP} = \frac{\Delta H^\circ}{\Delta S^\circ - R \ln P_{ext}} \quad (48)$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (49)$$

$$\Delta G = 0 \implies \Delta G^\circ = -RT \ln K_{eq} \quad (50)$$

$$\ln K_{eq} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (51)$$

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (52)$$

$$\ln \frac{P_1}{P_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (53)$$

$$K_a = \frac{[H]^+[A]^-}{[HA]} \quad (54)$$

$$K_w = [H]^+[OH]^- \quad \& \quad K_{w, 298 \text{ K}} = 1.00 \times 10^{-14} \quad (55)$$

$$pK_a = -\log_{10} K_a \quad (56)$$

$$K_{eq} = 10^{pK_{a, products} - pK_{a, reactants}} \quad (57)$$

$$pH = -\log_{10} [H^+] \quad (58)$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (59)$$

$$[A^-] \approx [HA] \implies pH = pK_a \quad (60)$$

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