FREE ENERGY 1E (SNEE)

Preston Snee
University of Illinois Chicago

Free Energy

Preston Snee

University of Illinois Chicago

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (https://LibreTexts.org) and like the hundreds of other texts available within this powerful platform, it is freely available for reading, printing and "consuming." Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects.

Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.

The LibreTexts mission is to unite students, faculty and scholars in a cooperative effort to develop an easy-to-use online platform for the construction, customization, and dissemination of OER content to reduce the burdens of unreasonable textbook costs to our students and society. The LibreTexts project is a multi-institutional collaborative venture to develop the next generation of open-access texts to improve postsecondary education at all levels of higher learning by developing an Open Access Resource environment. The project currently consists of 14 independently operating and interconnected libraries that are constantly being optimized by students, faculty, and outside experts to supplant conventional paper-based books. These free textbook alternatives are organized within a central environment that is both vertically (from advance to basic level) and horizontally (across different fields) integrated.

The LibreTexts libraries are Powered by NICE CXOne and are supported by the Department of Education Open Textbook Pilot Project, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptions contact info@LibreTexts.org. More information on our activities can be found via Facebook (https://facebook.com/Libretexts), Twitter (https://twitter.com/libretexts), or our blog (http://Blog.Libretexts.org).

This text was compiled on 03/10/2025

TABLE OF CONTENTS

15: The Hydrogen Atom

Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing***.

Acknowledgments

This textbook is a living instrument of learning due to the contributions of authors, editors and reviewers (including students!) who have participated in this project. We thank the University of Illinois at Chicago for providing seed money that got this textbook a start, especially Sandra deGroote and Ms. Janet Swatscheno.

Forward

What is the role of mathematics in Chemistry? We use math to reveal relationships that exist in nature that cannot be determined by any other reasonable means. Often Physical Chemistry is the last stop on the way to your degree, and you probably put this class off till last due to an irrational fear of mathematics. And while it may be true that calculus derivations are not your “thing”, if you’re good at this, you might get a better, higher paying job. So, it’s worth the effort.

CHAPTER OVERVIEW

1: Gas Equations of State

We power our planet by heat. That energy is largely derived (at the time of this writing in the early 2020's) from either burning fossil fuels or by setting off a continuous stream of controlled nuclear explosions under water. This creates hot, pressurized gas that turns a turbine that energizes a generator. Gas powered cars aren't that much different. This is how it works,with "it" being everything that holds our society together-cheap power.Understanding how power is generated important, and chemistry plays a significant role since we burn fuels to do it. For this book, we are going to start by understanding gases,especially hot gases, and how they create work. This will be, like, a totally lame chemical reaction:

$$\text{gas} + \text{heat} \rightarrow \text{hot gas} \rightarrow \text{work}$$

but it has the benefit of being very easy to understand. Later we will get to the burning fuel oil part, although I hope those chapters are deleted after something better comes along. If not, then those "Mad Max" movies are going to look more like documentaries from the future, and hopefully your hunting / gathering skills are up to speed.

References

Avogadro, "Essai d'une maniere de determiner les masses relatives des molecules elementaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons" Journal de Physique, **1811**, *73*, 58-76.

G.-J Su, "Modified Law of Corresponding States for Real Gases" Ind. Eng. Chem. **1946**, *38*, 803-806.

1.1: Units and the Perfect Gas Law

We need a way to calculate how much a gas (n = moles) is pressurized (P) when we heat it (T = temperature in Kelvin), which depends on the size of the container (V = volume). A lot of people have already had this idea, so much so that in the late 1600's Robert Boyle among others noted that pressure is inversely proportional to volume. Despite the fact that Boyle was more of an "alchemist" compared to a modern-day scientist, he had particularly good measuring equipment as shown in Figure 1.1 and was able to correlate pressure to volume over a range of 4× to demonstrate a near-perfect $P \propto \frac{1}{V}$ relationship. He used units of inches of mercury for the pressure because he used a mercury manometer for making measurements. It took another 200 years for Jacques Charles to discover that volume is proportional to temperature. He figured this out during his development of the first lighter-than-air balloon, having isolated hydrogen gas from the reaction of iron with acid. From there it took little time for Amedeo Avogadro to discover that, for gases at the same temperature and pressure, the gas's volumes are proportional to the gas's molecular weights. Most importantly he suggested that molecules are formed from atoms (this was new in the 1800's).

If we put this together we find:

$$PV \sim nT$$

but we have already run into a problem- the units are inconsistent! To see what we mean, let's start with pressure for which there are many units including inches of mercury, atmospheres, and bars. However, the standard S.I. unit of pressure is the Pascal, which is a Newton (a unit of force) per unit area (a meter squared, as the meter is the S.I. unit of length). Since a Newton is: $\frac{kg \cdot m}{s^2}$, then the Pascal is: $\frac{kg \cdot m}{s^2} \cdot \frac{1}{m^2} = \frac{kg}{s^2 \cdot m}$. When pressure is multiplied by volume in units of m^3 the result is in Joules: $PV = \frac{kg \cdot m^2}{s^2}$, which is energy. But nT is in units of mole·Kelvin, *which is not a Joule*. Thus, the equation: $PV \sim nT$ must be fixed to make the units work, which we will do by multiplying the right side by a constant "R" that simply divides out the mole·Kelvin and leaves energy behind as $\frac{J}{mol \cdot K}$:

$$PV = nRT \tag{1.1.1}$$

In the SI system the gas constant is specifically $R = 8.314 \frac{J}{mol \cdot K}$. Now we have Joules on the left and Joules on the right. In fact, this has to happen for every equation that describes a real system. There are three rules for the units of an equation:

1. The left and right sides of an equation must have the same units.
2. Terms in a sum must have the same units. For example, in the equation: $a \pm\ b\ = frac1c$, "a" and "b" have the same units.
3. Terms in an equation multiply or divide into different units. Applying this to the above, term "c" has the inverse units of "a" and "b". Numbers like \piup or 2.0 have no units at all.

Getting back to task, does $PV = nRT$ look familiar? Of course! It is the perfect gas equation that you learned about in high school. Hence, we have an equation for solving the pressure generated by a hot gas, which we will use to calculate the energy of an expanding piston inside a car engine. But is $PV = nRT$ a "perfect" equation? I think not- and here is how you can tell. You are probably aware that molecules comprise the moles of gas in $PV = nRT$, and I wouldn't expect all gas molecules to behave the same way. For example, take water at room temperature and pressure. How can $PV = nRT$ be correct, after all water is a liquid! Here is a better example- trimethyl indium (InMe_3) can spontaneously explode in the gas phase, but I don't see that behavior in $PV = nRT$! Basically, the problem is that there is no input into the perfect gas equation for what the gas is which is clearly important, so the perfect gas law must be an approximation.

1.2: Van der Waals Equation

People figured out that the perfect gas law was far from perfect back when horseback riding was still a mode of transportation. In 1881 Johannes van der Waals realized that the perfect gas law can be derived from another set of relationships that govern energy, so long as the gas molecules cannot interact with each other. This also implies that the gas atoms do not collide and that the molecules do not have their own volume. As a result, he inserted two parameters (” a ” and ” b ”) to the perfect gas equation to describe gas behavior more realistically:

$$P = \frac{nRT}{V - n \cdot b} - \frac{n^2 \cdot a}{V^2} \tag{1.2.1}$$

This is called a real gas equation and applies to “real gases” as opposed to an “unreal” perfect gas. The ” a ” and ” b ” parameters are unique for every gas and are determined from experimental data. But do these constants mean anything? Let’s first study the ” a ” parameter by eliminating ” b ” (we set it equal to 0 m^3/mol) and we find that: $P_{real} \approx \frac{nRT}{V} - \frac{n^2 \cdot a}{V^2}$. Next, subtract the perfect gas equation $P_{perfect} = \frac{nRT}{V}$ from it:

$$P_{real} - P_{perfect} \approx \frac{nRT}{V} - \frac{n^2 \cdot a}{V^2} - \frac{nRT}{V} = -\frac{n^2 \cdot a}{V^2}$$

Therefore, the difference between the van der Waals equation (with b = 0 m^3/mol) and the perfect gas equation is: $\Delta P = -\frac{n^2 \cdot a}{V^2}$. Since the van der Waals ” a ” parameter is positive for all known gases, this shows that the ” a ” parameter’s role is to make a real gas’s pressure less than a perfect gas because ΔP is always negative. Notice how the difference $-\frac{n^2 \cdot a}{V^2}$ can be much bigger if V is small, which happens if you have a lot of gas at a very high pressure. These effects are shown in Figure 1.2, which is the perfect gas pressure and van der Waals pressure for CO$_2$ under various conditions. It can be seen that the real gas pressure is lower than that predicted by the perfect gas law.

Now imagine that you’re at your 1st Physical Chemistry exam and are asked to describe why that might be (this is probably going to happen!). Recall that van der Waals knew that gas molecules must not interact with themselves nor occupy any volume for $PV = nRT$ to work. Would a real gas molecule’s ability to interact with itself decrease the real pressure? Or perhaps the real pressure is modulated due to fact that the gas molecules occupy some of the volume (this would likely raise the pressure)? Hopefully your intuition leads you to believe that the ” a ” parameter is associated with a gas molecule’s ability to interact among themselves, which would lower the pressure. This is like gravitational attraction that keeps our solar system together- without gravity all the planets, stars and asteroids would all fly apart from each other as though they were gas molecules at high pressure suddenly released from the container!

Gas	**a** (kPa· L^2/mol^2)	**b** (L/mol)	**P$_c$** (atm)	**T$_c$** (K)
He	3.46	0.0238	2.23	5.18
H_2	24.76	0.02661	12.8	33.2
N_2	137.0	0.0387	33.4	126
Xe	425.0	0.05105	57.6	290
O_2	138.2	0.03186	49.8	155
CH_4	228.3	0.04278	45.0	188
CO_2	364.0	0.04267	73.1	304
H_2O	553.6	0.03049	218	647

The meaning of the ” b ” parameter can be determined by unit analysis. This is one reason that units are emphasized here, because you can often use them to answer questions! This also gives us a challenge problem- what are the units of ” b ” given the following:

$$\frac{nRT}{V-n\cdot b} \propto \frac{J}{m^3-mol\cdot b}$$

Based on the previous discussion, hopefully you realize the Joule doesn't matter, rather the $n \cdot b$ term must have units of m^3 (the same as V) since they are members of a summation; note subtraction is just the addition of a negative quantity. Some middle school algebra reveals that " b " has units of m^3/mol and represents the volume of the actual gas molecules. You might have noticed the units of " b " were stated on the previous page- try to pay more attention!

There is another way to determine what " b " represents, which is to find what the volume of the van der Waals gas at high pressure. To derive this, first take the van der Waals equation, bring the " a " term to the right:

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

and then multiply by $V-n\cdot b$:

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

Now divide out by the left hand $P+\frac{a\cdot n^2}{V^2}$ term and take the limit of high P:

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

On the right-hand side, we see that there is a finite nRT term divided by a very large number (P), which makes me think the limit is 0 m^3. Before we make this conclusion we need ask what can $\frac{a\cdot n^2}{V^2}$ do to mess up the limit? To answer, first let's ask ourselves how can P get infinitely big? Why, by making V infinitely small, resulting in $\frac{a\cdot n^2}{V^2}$ becoming very big (just like P!). Thus, we can safely conclude that $\frac{nRT}{\left(P+\frac{a\cdot n^2}{V^2}\right)} \;=\frac{nRT}{(\infty+\infty)}=0\ m^3$, and thus:

$$(V-n\cdot b) \;=0\ m^3$$

or better yet the van der Waals b term is equal to $\frac{V}{n}$, the volume per mole under extremely high pressure. As most gases will solidify is put under enough pressure, and a solid's volume is fully occupied by the "bodies" of the molecules, we now see that " b " is the per molar volume of the actual molecules and is not related to the size of the container (V) that they reside in.

1.2.1 Compressibility Factor. How necessary is the use of a real gas equation such as the van der Waals? This is the same as asking, how "bad" is the perfect gas law for describing real gases? To answer this question, we introduce a unitless metric called the compressibility factor "Z":

$$Z=\frac{P_{real}}{P_{perfect}}=\frac{P_{real}V}{nRT} \tag{1.2.2}$$

Compressibility is a fraction for which Z = 1.0 if a real gas behaves like a perfect one. Shown in Figure 1.3A are values for Z for nitrogen gas over a temperature and pressure range of 140 K to 300 K and 8 atm to 260 atm, respectively. Here we see that Z can deviate substantially from 1.0, usually being less than 1.0 and reaching the lowest value of 0.406 at 140 K at a perfect gas pressure of 65 atm. How do you to interpret these data? For example, a compressibility factor less than 1.0 means that $P_{real}V$ is less than nRT, but is it the pressure or volume that is "too small"? Since these measurements were likely made in a thick, solid metal container, the volume of which doesn't vary no matter the temperature and pressure of the gas inside of it, we assign the compressibility factor to pressure. What this means is that, if Z = 0.406, then the measured real pressure of N_2 gas is 26.4 atm *when it should have been 65 atm* if it behaved like a perfect gas and its pressure was the same as $\frac{nRT}{V}$. Likewise, Figure 1.3C shows that helium's compressibility can be much greater than 1.0, and thus the pressure is "too high". As can be seen, real gases can have substantial deviations from perfect gas behavior.

imageThe van der Waals equation can be used to estimate the compressibility factor. Starting with $P=\frac{nRT}{V-n\cdot b}-\frac{n^2\cdot a}{V^2}$, we multiply both sides by $\frac{V}{nRT}$:

$$\frac{PV}{nRT} = Z = \frac{V}{V - n \cdot b} - \frac{a \cdot n}{RTV} \tag{1.2.3}$$

which reveals that Z is increased by the effect of the molecular volume (the " b " parameter) because " b " is always positive and thus $\frac{V}{V-n \cdot b} \geq 1.0$. The attractive forces (the " a " parameter) can only lower Z. As can be seen in Figure 1.3A and C, Z is usually less than 1.0 for nitrogen but generally greater than 1.0 for helium. The latter behavior is generally only observed with H_2, He, and Ne, while all other real gases behave like N_2. Examination of the van der Waals constants for these gases on Table 1.0 shows that H_2, He, and Ne have very low " a " values. Thus, H_2, He, and Ne are more like hard billiard balls that are constantly cracking against each other. This is not true for most real gases like N_2, CO_2 and CH_4; their behavior is dictated more by their self-attraction via the \(``a")parameter. Furthermore, note that the low value of N_2's Z seen in Figure 1.3A occurs when the gas is cold and under high pressure, where it is close to liquifying. Of course the perfect gas equation is way off under these conditions! "

Shown in Figure 1.3B are the calculated Z's for N_2 gas using the van der Waals equation. As can be seen, this real gas equation generates a reasonable representation of the behavior of N_2, but it's not perfect. This is because the van der Waals equation ultimately tries to predict very complex, at times quantum mechanical behavior using just two empirically fitted parameters. Of course it isn't perfect! But clearly superior to the perfect gas law, which is represented by a flat plane at Z=1.0. And good enough for van der Waals to win the Nobel Prize in Chemistry in 1911.

1.3: The Virial Equation

Speaking of the inaccuracies of the van der Waals equation, when applied to the compression factors for helium shown in Figure 1.3C the van der Waals equation is substantially in error. Now engineers, who must make sure things like boilers and nuclear reactors don't explode, must have very accurate equations of state and thus sometimes the van der Waals relation doesn't cut it. In this regard, one way to accurately fit data is to use a series expansion. For example, let's rewrite the compression factor for the perfect gas law as: $\frac{PV}{nRT}=1$, but now expand the right side of the equation in a power series of the molar density $\frac{n}{V}$:

$$\frac{PV}{nRT}=1.0+B(T)\cdot\left(\frac{n}{V}\right)+C(T)\left(\frac{n}{V}\right)^2+\ldots \tag{1.3.1}$$

This is the Virial equation of state, where the inclusion of an increasing number of B, C, … etc. terms multiplied by powers of $\left(\frac{n}{V}\right)^{1,2\ldots}$ can arbitrarily increase the accuracy (although typically one does not see the series go beyond the $C(T)$ term). At first, it would appear that the Virial is not better than the van der Waals, as both only have $\sim$2 additional parameters to rectify the perfect gas law. However, did you notice that the Virial parameters $B(T)$ and $C(T)$ are temperature dependent whereas the van der Waals parameters are not? As a result, the Virial is substantially more accurate than the van der Waals equation, which is why we used it to model the compression factor of helium in Figure 1.3D. Clearly the Virial does a good job representing helium gas over a range of temperatures and pressures. As a result, we have demonstrated that a series expansion can always be used to create a better fit to experimental data, although hopefully you already knew that.

1.3.1 Residual Volume

We have discussed at length the physical basis for the two van der Waals parameters and how they influence the compressibility factor Z. What about the Virial? Do the $B(T)$ and $C(T)$ terms have any meaning like the van der Waal's $``a''$ and $``b''$ constants? Unfortunately, such analysis isn't as straightforward, and we have to develop another method for quantifying the (im)perfections of a gas. In this regard, we introduce the residual volume, which is the difference in the per molar volume $\left(\frac{V}{n}=V_m\right)$ of a real gas minus the same of a perfect gas under very low pressure (or high volume) conditions, i.e.:

$$res.\ volume=(V_{m,real}-V_{m,perf}) \tag{1.3.2}$$

The reason that a limit is applied (either $P\rightarrow 0$ Pa or $V_m\rightarrow\infty$ m^3/mol) is that real gases behave much more like a perfect gas under these conditions. Hopefully the reasons are obvious- for a limited number of gas molecules in a very large volume container, they do not have much opportunity to interact nor collide. As a result, it is true that $\left(\frac{PV_m}{RT}\right)=1.0$. However, what about the difference \(\left(V_m-\frac{RT}{P}\right))? This is the definition of the residual volume, and at first it appears that it should be 0 m^3/mol. Let's check this with a derivation, starting with Equation 1.5:

$$\frac{PV}{nRT}=1.0+B(T)\cdot\left(\frac{n}{V}\right)+C(T)\left(\frac{n}{V}\right)^2$$

First, factor $\frac{RT}{P}$ throughout:

$$\frac{V}{n}=V_m=\frac{RT}{P}+B(T)\cdot\left(\frac{nRT}{PV}\right)+C(T)\frac{n^2RT}{PV^2}$$

and then bring $\frac{RT}{P}$ to the left:

$$V_m-\frac{RT}{P}=B(T)\cdot\left(\frac{nRT}{PV}\right)+C(T)\frac{n^2RT}{PV^2}$$

And apply the limit as follows:

$$\left(V_m-\frac{RT}{P}\right)=\left(B(T)\cdot\left(\frac{RT}{PV_m}\right)+C(T)\frac{RT}{PV_m^2}\right)$$

Now here we have a problem. If $V_m\rightarrow\infty$ m^3/mol then P→0 Pa, so what do we do with PV_m? Does it get infinitely big, or disappear to 0 Pa•m^3, or maybe it doesn't change at all? Here, we use the fact that $\left(\frac{PV_m}{RT}\right)=1.0$, which means we can replace every PV_m with RT:

$$res.\ volume=\left(B\left(T\right)\cdot\left(\frac{RT}{RT}\right)+C\left(T\right)\frac{RT}{RT\cdot V_m}\right)\ =B\left(T\right)$$

Since the RT term is not affected by the limit of increasing volume or equivalently decreasing pressure, the $B\left(T\right)$ term survives while the $C\left(T\right)$ term is removed by the remaining V_m factor that becomes infinitely large. As a result, we can see that the residual volume of a real gas is not 0 m^3/mol, and in fact it is defined by the Virial $B(T)$ parameter.

Since we are here discussing residual volume, how about we use the van der Waals equation for the same purpose? Starting with Equation 1.2: $P=\frac{nRT}{V-n\cdot b}-\frac{n^2\cdot a}{V^2}$, first multiply everything by $\frac{(V-n\cdot b)}{nP}$ as follows:

$$\frac{\left(V-n\cdot b\right)}{n}=\frac{RT}{P}-\frac{n\cdot a\left(V-n\cdot b\right)}{PV^2}$$

Now do some factoring and note that $\frac{V}{n}=V_m$:

$$V_m-b=\frac{RT}{P}-\frac{n\cdot a}{PV}-\frac{n^2\cdot a\cdot b}{PV^2}$$

Rearranging $\frac{RT}{P}$ and b with application of the limit yields:

$$\left(V_m-\frac{RT}{P}\right)\ =res.\ volume=\left(b-\frac{a}{PV_m}-\frac{a\cdot b}{PV_m^2}\right)$$

Here, we run into the same problem of what to do with the multiple PV_m terms, but as before we will replace them with RT:

`res.\ volume=\left(b-\frac{a}{RT}-\frac{a\cdot b}{RTV_m}\right)\ =b-\frac{a}{RT}            \\label{1_7_}`

Thus $\frac{a\cdot b}{PV_m^2}\rightarrow 0$ as $V_m\rightarrow\infty$. So we see that the difference between a real gas volume and a perfect gas volume is that the real gas has extra space taken up by the gas molecules (as defined by the " b " parameter), while the attractive forces work like gravity as they cause the molecules to coalesce to reduce the volume.

1.4: Phase Transitions

Under certain temperature and pressure conditions real gas equations can predict very odd behavior. We will use CO_2 as an example because it has interesting properties that makes it useful for a large number of industrial applications. The phase diagram of CO_2 is shown in Figure 1.4, where a “critical point” is marked with a red “×”. This is where the distinction between the liquid and gas phases comes to an end. Furthermore, above the critical temperature it is impossible for the gas to be liquefied even if you pressurize the system considerably. This high pressure and temperature supercritical region should be considered a separate phase because it can have unique properties that are not observed for either the gas or liquid phases. For example, supercritical CO_2 is a very good solvent; in fact, it is used to extract the caffeine out of coffee beans.

The van der Waals equation predicts critical behavior. Shown in Figure 1.5 are van der Waals P vs. V_m isotherms, where each line represents the pressure at a single temperature (the top line is 70.9 $^\circ$C and the bottom one is -8.9 $^\circ$C). Do you see how the green line at 30.9 $^\circ$C flattens out near 73 atm? Now look back at Figure 1.4- that’s the critical point! In fact, we can mathematically define the critical point because it’s clear that the line is flat, i.e. $\frac{\partial P}{\partial V_m} = 0\ atm \cdot mol/L$. In fact, its true that the double derivative is also flat: $\frac{\partial^2 P}{\partial {V_m}^2} = 0\ atm^2 \cdot mol^2/L^2$. Setting these two derivatives equal to 0 provides two equations that can be used to solve the two unknowns, which are the critical pressure $P_c = \frac{a}{27b^2}$ and per molar critical volume $V_{c,m}$ = 3b. Several examples are provided in Table 1.0. When we plug P_c and $V_{c,m}$ into the van der Waals equation we determine that $T_c = \frac{8a}{27R \cdot b}$.

Now let’s look at the P vs. V_m isotherms in Figure 1.5 further, because at temperatures below T_c there is some odd behavior circled with “?”s. Specifically, it appears that an increase in volume results in an *increase in pressure*- how could this possibly be true? Do you think if you were to pull on a piston that it would suddenly fly out toward at you? No, this would never happen. Thus, it appears that the van der Waals has some certain pressure, volume, and temperature points where it does not describe gases correctly. To understand what is happening, imagine that we have a container filled with CO_2 at a set of P, V_m and T in the circled region of Figure 1.5. If we peer through a window into this container we would make a startling observation - the CO_2 is a liquid! So, of course the real gas equation doesn’t make sense anymore because CO_2 isn’t a gas to begin with!

Perhaps we can use this fact to determine at what pressures and temperatures that the gas liquifies and check that against the phase diagram? To do so we need to be able to define the positions in the P vs. V_m isotherms that the gas is expected to liquify. This is possible by the creation of a “Maxwell construction”, which is meant to blot out the offending increasing P vs. V_m behavior with a straight line. An example is shown in the inset of Figure 1.5, where the Maxwell construction is the thick green line that cuts through the weird part of the van der Waals isotherm at -8.9 $^\circ$C. To understand, imagine that we have a container at -8.9 $^\circ$C, the V_m is 0.073 L/mol, and the pressure is 40.6 atm (the furthest left-hand point of the Maxwell construction in Figure 1.5 inset). If we decrease the volume further the pressure increases dramatically. It turns out that the reason for this is that the CO_2 is a liquid. Of course it takes extremely high pressure to compress a liquid! Now let’s move right of this point by increasing the volume, and as we do so the Maxwell construction dictates that the pressure remains a constant 40.6 atm. This is happening because the liquid inside the container is turning into a gas, which maintains the pressure despite the increasing volume. This goes on until we reach V_m=0.36 L/mol, the furthest right-hand point of the Maxwell construction in Figure 1.5 inset. Here, the liquid has completely vaporized, and so if we keep increasing the volume then the pressure drops just like a normal gas.

For a given isotherm there is one line that defines the Maxwell construction. This corresponds to a single pressure because the construction is a straight line. The pressure of the Maxwell construction is unique for each isotherm shown in Figure 1.5 as it is defined such that the areas of the van der Waals isotherm above and below the line are equal. These are the grey shaded areas in the inset of Figure 1.5. We determined a set of temperatures and corresponding pressures and plotted them as the green circles in Figure 1.4. The critical point is dead on, and clearly the other data track the liquid / vapor line decently well. Nay Sayers may note how the points are not perfect; let me remind you that the van der Waals equation is for gases. Yet it predicts the formation of the liquid phase, and the predictions in Figure 1.4 are pretty good! And did your Nobel-winning real gas equation do better?

1.5: Corresponding States

The fact that the critical point is unique for each gas provides a way to create a real gas law that applies to all gases. To do so, we first define what are called reduced units, which are $P^* = \frac{P}{P_c}$, $T^* = \frac{T}{T_c}$, and $V^* = \frac{V_m}{V_{c,m}}$, where P_c, T_c, and $V_{c,m}$ are the critical pressure, temperature, and per molar volume, respectively. Note that we can cleverly determine pressure from the reduced pressure via: $P = P^* \cdot P_c$ and likewise for temperature and per molar volume. Now take the van der Waals equation where we absorb n into V (the per molar form): $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$ and insert P, V$_m$, and T as in the above example:

$$P^* \cdot P_c = \frac{R \cdot T^* \cdot T_c}{V^* \cdot V_{c,m} - b} - \frac{a}{(V^* \cdot V_{c,m})^2}$$

Now the trick is that we know what the critical values of pressure, temperature and volume are from our previous discussion. Plug these into the above and we find:

$$P^* \frac{a}{27b^2} = \frac{R \cdot T^* \frac{8a}{27Rb}}{V^* \cdot 3b - b} - \frac{a}{V^{*2} \cdot 9b^2}$$

While painful, the use of middle school algebra yields the following: $P^* = \frac{T^* 8ab}{a \cdot (V^* \cdot 3b - b)} - \frac{27b^2 a}{a \cdot V^{*2} \cdot 9b^2}$ which is further reduced into:

$$P^* = \frac{8T^*}{3V^* - 1} - \frac{3}{V^{*2}} \tag{1.5.1}$$

image You are probably thinking- so what? There is a subtle property of the reduced form of the van der Waals equation of state- there are no a or b coefficients! And since these are unique to every gas, the reduced van der Waals equation applies to *every* gas.

To demonstate how this is true, plotted in Figure 1.6 are the compression factors for 10 gases as a function of their reduces pressures and temperatures. Clearly the data cluster along similar isothermal lines, which reveals that they have fundamentally similar interactions as revealed by reduced real gas equations of state. However, as in the case of predicting the compression factor of helium gas shown in Figure 1.3, the van der Waals does not accurately reproduce the data shown in Figure 1.6. Instead, we have used the Redlich-Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} \cdot V_m (V_m + b)} \tag{1.5.2}$$

which differs from the van der Waals in how the attactive forces are minimized by the $\frac{1}{\sqrt{T}}$ temperature factor in the $``a''$ term. This has been shown to substantially increase the accuracy of the equation in the supercritical regions of the phase diagram. Last, there are a multitude of other, even more complex equations of state incorporating even more emperical constants and higher order terms. One should realize that, mathematically, it is impossible to not realize greater accuracy using longer equations with more parameters. If this is one's end goal, then great; however, it is questionable whether one gains physical insight into the underlying mechanisms of molecular-molecular interactions, which is the goal of Physical Chemistry.

Conclusion. We have shown here that the perfect gas law isn't all that perfect. Deviations from such a simple equation are expected based on the identity of the molecules that make the gas. The van der Waals and Virial equations account for much of this behavior, which can be understood by the fundamental properties of the molecules that comprise the gas. Specifically, that molecules are generally attracted to each other, but if the get too close then collisions occur! As will be demonstrated in later chapters, these real gas behaviors modify thermodynamic processes, and are responsible for some important applications such as refrigeration.

CHAPTER OVERVIEW

2: Energy

Here we inquire into the nature of energy in our next step on learning thermodynamics. Energy is probably one of the earliest words a person learns, so of course we know what it is! However, do we have a robust understanding that can be the subject of experimentation? And if so, do the experiments actually answer the questions put forth? Here is the problem- if I ask you to do an experiment to resolve "what is energy," you will propose measuring a change in energy, and not energy itself. Some of you may cry foul for having learned that energy per mole of a chemical can be defined by the Equipartition Theorem (discussed in Sec. 2.4 in case you haven't heard of it before):

$$U_m = \frac{1}{2}RT \cdot (degrees\, of\, freedom) \tag{2.1}$$

where we will call energy "U" for now, and the "m" subscript stands for "per mole". A degree of freedom is something like the vibration of a H_2 molecule or the ability of argon gas to translate in three dimensions. Certainly energy must exist if we have an equation for it! However, temperature is measured on the absolute Kelvin scale. As a result, I would contend that the Equipartition theorem does not provide an equation for energy, rather, it dictates the energy difference between something at temperature T relative to that same thing at 0 K.

Let's try again! What about Einstein's famous equation whereby energy is equal to mc^2, which describes how nuclear reactors generate electricity? Actually, mc^2 can be thought of as the energy difference between a state with mass compared to one with no mass. All of this is making me think that there may be no "energy" at all! Rather, there is only a change in energy; perhaps the subject of "what is energy" is more a problem for philosophers than for physical chemistry students. Furthermore, as you will learn in Chapter 4, we should not be concerned with energy at all as entropy is more important.

2.1: Work and the Inexact Differential

2.1 Changes of energy: work and heat

Now that we are content with measuring changes in energy, we can start by defining it with:

$$\partial U = \partial w + \partial q \tag{2.1.1}$$

where the change in energy (∂U) is equal to the change in heat (∂q) plus the change in work (∂w). The symbol "∂" indicates a partial differential, which should be familiar to you from your first Calculus class. It represents a change so small that it is essentially ~ 0; as a result, partial quantities must be integrated to build up a "body" so that the difference can actually be measured. Throughout this course, we will often see that calculus equations can be described using physical actions, which must be true as the variables are real things. For example, integrating moles: $\int_{0\ mol}^{n\ mol} \partial n$ physically corresponds to leaking **n** moles of a gas into a vacuum chamber. Likewise integrating volume: $\int_{0\ m^3}^{X\ m^3} \partial V$ is akin to filling a hole. We will point out such analogies when possible, and hopefully it will help you understand the calculus equations we will work with throughout the remainder of the book. Last, you should know that partials have units. Thus, $\partial n sim\ 0\ mol$ and $\partial V sim\ 0\ m^3$, not just "0".

There is a small complication that we run into when performing thermodynamic integrations. Specifically, the partial differential "∂" may represent a change along a particular path and integrating that partial will have to take the path into account. But before we start losing everyone in "math-speak", note that you are already familiar with paths! For example, you can work efficiently or inefficiently; these are different paths. The integration along an inefficient path will reveal that less work comes out of the system compared to the efficient one.

Heat is rather boring, except to pyromaniacs. It represents energy transfer, like lighting a match under a metal can when you were learning calorimetry in Freshman chemistry (Figure 2.1A). This was rather inefficient due to irreversible losses to the environment; however, heat can be provided to a system very efficiently as shown in Figure 2.1B. Like work, efficient heating is the best, and for the purposes of this class, heat is mostly expressed as the addition of "X" Joules of energy into a gas in a piston or a water cup. Like we said, boring. Now take the same thing and divide by temperature, as discussed in Chapter 4, and you will understand why everything in the Universe works the way it does. Including cats.

Let's calculate the work ∂w due to a change in volume of a piston inside your car engine. This occurs immediately after the exterior pressure increases after the spark plug ignited the fuel/air mixture:

$$\partial w = -P_{ext} \cdot \partial V \tag{2.1.2}$$

This is the IUPAC definition of volume work, whereby the piston is considered the system (alternatively, some view the exterior vehicle as the system- we don't do that here!). Work done ***on the system*** requires lowering the interior volume. This would occur by increasing the exterior applied pressure P_{ext}, as this is the driver of the volume decrease. Note that the piston compression will stop when the interior and exterior pressures are equal. Work done ***on the system*** is positive energy, because the "–" sign in $-P_{ext} \cdot \partial V$ negates the loss of volume ∂V, which is negative. No work is done if there is no change in volume, even if the external pressure is significantly higher than the piston's internal pressure. Negative work performed ***by the system*** occurs when the piston expands; both positive (compression) and negative (expansion) work by a piston are diagrammed in Figure 2.2 above.

Work is path-dependent because it can be performed efficiently or inefficiently. Just like how we can raise a weight using a simple machine such as a pulley, or by brute force pushing the same weight with our bare hands and legs. There is a mathematical representation of this path dependence, and to demonstrate let's analyze two different ways for work to be done on a piston. This is usually referred to as "PV-work". Step 1 of figure 2.3 represents inefficient compression whereby the external pressure jumps immediately from 1 to 2 bar. As in our previous example, a model for such a dynamic is the interior of a car engine piston that experiences a sudden pressure jump due to the spark plug igniting gasoline; however, we will assume that the temperature is constant since this significantly simplifies the analysis. After the exterior pressure increase, the system "catches up" in step 2 by compressing the piston. Since the equation for work: $\partial w = -P_{ext} \cdot \partial V$ has two partials (∂w and ∂V), we need to integrate both to define a finite, measurable value for work:

$$\int \partial w = \Delta w = \int -P_{ext} \cdot \partial V \tag{2.1.3}$$

First, we must make sure the units are consistent with Joules. Since volume is often expressed in Liters (equivalent to cubic decimeters), we must change the pressure to kPa since kPa×L=J. Next, we have to use definite integrals by applying limits, and note that there are two steps in the compression. In these situations, the total work is the sum of the integrations along each step. In the first, we see that the exterior pressure increases while the volume is constant. As a result the work is:

$$\Delta w_1 = \int_{2L}^{2L} - P_{ext} \cdot \partial V = -P_{ext} \times (2L - 2L) = 0\ J$$

There is no work done in the 1st step because it doesn't matter what the pressure is doing if it gets multiplied by $\Delta V_1 = 0\ L$. Now the second step where the volume does change the work is integrated as:

$$\Delta w_2 = -P_{ext} \int_{2L}^{1L} \partial V = -200\ kPa \times (1L - 2L) = +200\ J$$

where the exterior pressure comes out of the integral because it is constant. The total work is the sum of these two steps, which is a positive 200 Joules.

Let's see what happens if we do the work efficiently, which means that we slowly increase the exterior pressure from 1 to 2 bar. This allows the internal pressure enough time to equalize incrementally to the rising exterior pressure as shown in Figure 2.4. We will describe this using a "phenomenological" model, which is a mathematical expression that makes sense. In this case, we will say that the interior volume decreases from 2 L to 1 L as the exterior pressure increases from 100 kPa to 200 kPa as: $V = 2L \cdot \frac{100\ kPa}{P_{ext}}$. The change in volume is now a smooth function of the exterior pressure, although we actually need to solve this model for the exterior pressure: $P_{ext} = 100\ kPa \cdot \frac{2\ L}{V}$ because the exterior pressure explicitly appears in the equation for work: $\partial w = -P_{ext} \cdot \partial V$. What is interesting is that P$_{ext}$ is now "hiding" a factor of V which is our integrand ∂V. As a result, we must include this volume factor in the evaluation of the integral, which we do by solving:

$$\Delta w = \int_{2L}^{1L} -P_{ext} \cdot \partial V = \int_{2L}^{1L} \frac{-100\ kPa \cdot 2\ L}{V} \cdot \partial V$$

This integral is more complicated than in the previous example, but fortunately we know enough Calculus to solve this by taking out constant factors and using the identity: $\int x^{-1} \partial x = \ln(x)$:

$$\Delta w = -100\ kPa \cdot 2L \cdot \int_{2L}^{1L} \frac{\partial V}{V} = -100 kPa \cdot 2L \cdot \ln\left(\frac{1L}{2L}\right) = 138\ J$$

Consequently, the efficient transition involves slowly increasing the exterior pressure to allow the interior pressure to adjust accordingly, which requires less positive work ($\Delta w = 138$ J). In contrast, the inefficient transition has such a sudden increase in the exterior pressure that the system doesn't have time to respond, which ultimately necessitates greater, more positive work ($\Delta w = 200\ J$). Hence, there is a path dependence to work. Note that, in either case the piston reached the same final state, although the efficient path required less work to achieve it.

2.2: Reversible and Irreversible Transitions

We now introduce another set of words for the path dependence of work, that being reversible for the efficient path and irreversible for the inefficient. The origins of the “reversible” terminology will be made clear later, but in the meantime, let’s understand how to maximize the work out of a system. Figure 2.5 will help us understand the difference by studying how a piston expands. Expansion work, or negative work ***out of a system***, is generally considered “useful” because we design our machines to push things along. After all, you don’t feel that your car is dragging you behind it, do you? We will show here that reversible expansion work is the most negative work out of a machine and is the most efficient. We start with a piston under external compression and then turn down the external pressure (P_{ext}) by a very small amount. The interior pressure (P) of the piston is allowed to equilibrate with the exterior pressure before the exterior pressure decreases again. Thus, $P_{ext} = P$. This is important because, as in the previous example, the exterior pressure in the work equation is “hiding” a factor of volume in it since $P = \frac{nRT}{V}$ if we assume perfect gas behavior. The volume factor is part of the integral (equation 2.4) as shown here:

$$\int \partial w_{rev} = \Delta w_{rev} = \int -P_{ext} \cdot \partial V \ P_{ext} = P \rightarrow int - P \cdot \partial V \ P = \frac{nRT}{V} \rightarrow int \frac{-nRT}{V} \cdot \partial V$$

Now we must set limits, and note that n, R and T are constant and can be removed from the integral:

$$\Delta w_{rev} = -nRT \cdot \int_{V_i}^{V_f} \frac{\partial V}{V} = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right) \tag{2.2.1}$$

One interesting thing about this equation is that, for small changes in volume: $\ln\left(\frac{V_f}{V_i}\right) \approx \frac{V_f - V_i}{V_i} = \frac{\Delta V}{V}$. Consequently, work is proportional to the fractional change in volume times some constants that give it units of Joules; hopefully this will make remembering this equation easier.

Irreversible work is much easier to calculate because there is a sudden change in the exterior pressure that occurs before the system can respond. As a result, P_{ext} can be removed from the integral (equation 2.4) as:

$$\Delta w_{irrev} = -P_{ext} \cdot \int_{V_i}^{V_f} \partial V = -P_{ext} \cdot \Delta V \tag{2.2.2}$$

To demonstrate, Figure 2.5 represents the expansion work by the shaded area under the curve for both the reversible (blue, single hatch) and irreversible (red, cross hatch) paths. We can present work this way because integrals are areas under curves. We see that the reversible region encompasses the irreversible, and as such the area under the reversible expansion is greater than the irreversible. And due to the negative sign in the work equation: $\partial w = -P_{ext} \cdot \partial V$, the reversible process generates the most negative work possible.

On the next page are a series of examples of a piston that is compressed and then expands to help solidify your ability to perform calculations on isothermal reversible and irreversible work. Example problems 2.1 & 2.2 show that an irreversible compression / expansion cycle *consumes* a positive quantity of work. Note that we state *consumes* because the work is performed *on the system*, the energy from which comes quite literally from you. In contrast, example problems 2.3 & 2.4 show that the sum of the work due to reversible cycle is 0 J. This is in fact the origin of the word “reversible”, as opposed to the irreversible situation in

---

2.3: Exact and Inexact Partials and Euler’s Test

Before we leave the subject of work, there is a property of path-dependent differentials like ∂w and ∂q that needs to be examined using multivariable calculus. Normally the change in a function $f\left(x\right)$ is $\frac{\partial f}{\partial x}$; however, when the function has two or more variables, i.e. $f\left(x,y\right)$, we must analyze the change in the function with respect to both x and y as: $\partial f\left(x,y\right)\approx\frac{\partial f}{\partial x}+\frac{\partial f}{\partial y}$. Now being good chemists, we know that if we are measuring the change in an observation (∂f) due to a change in an experimental condition (∂x), we then need to hold all other variables (here, y) constant and vice versa. To represent this, we change the notation as: $\partial f\left(x,y\right)\approx\left(\dfrac{\partial f}{\partial x}\right)_y+\left(\dfrac{\partial f}{\partial y}\right)_x$. However, this expression can’t be fully correct as ∂f has the same units as the function f while $\left(\dfrac{\partial f}{\partial x}\right)_y$ has units of $\frac{f}{x}$. Another clue that something isn’t quite right is that fact that ∂f is infinitesimally small, yet $\frac{\partial f}{\partial x}$ is finite.

”The solution is that the real partial is:

$$\partial f\left(x,y\right)=\left(\dfrac{\partial f}{\partial x}\right)_y\partial x+\left(\dfrac{\partial f}{\partial y}\right)_x\partial y \tag{2.3.1}$$

which is tantamount to calculating a change in the function (∂f) by following $f\left(x,y\right)$ in small steps (∂x) along the x-direction in an amount weighted by the slope $\frac{\partial f}{\partial x}$, and then doing the same in the y-direction as shown in Figure 2.6. To apply the lesson above, the partial of the function $f\left(x,y\right)=x\cdot y$ is:

$$\partial f\left(x,y\right)=\left(\dfrac{\partial x\cdot y}{\partial x}\right)_y\partial x+\left(\dfrac{\partial x\cdot y}{\partial y}\right)_x\partial y=y\cdot\partial x+x\cdot\partial y \tag{2.3.2}$$

This is an example of an exact differential, which means that there is a function $f\left(x,y\right)$ associated with $\partial f\left(x,y\right)$. Such a differential is said to be exact, and it is ***not path dependent***.

Thermodynamic variables that are exact include energy and entropy, but not work or heat as we have already shown that they depend on whether a process is reversible or irreversible. Since energy and entropy are not path dependent, we call them state variables, which means that their values are not derived from how the state came to exist. For example, the potential energy of a cat on a bookshelf is due to gravity and is a function of the height of the shelf. It doesn’t matter how the cat got there, only that it is there! Hence, state function.

Inexact differentials are the opposite of the exact. An example is: $\partial f\left(x,y\right)=x\cdot\partial y$. This is ~1/2 the exact differential in Equation 2.8, and as a result you could never write a function $f\left(x,y\right)$ that could be differentiated into $\partial f=x\cdot\partial y$. Work: $\partial w\left(P_{ext},V\right)=-P_{ext}\cdot\partial V$ is clearly inexact because it is identical to: $\partial f\left(x,y\right)=x\cdot\partial y$, the letters are just different! This is why you haven’t seen us write w =…, because work is only defined as a differential ∂w. As a result, work is path dependent and is ***not a state variable***.

Euler (pronounced Oiler!) introduced a test to examine whether a differential $\partial f\left(x,y\right)$ is exact or not:

\left(\dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x=\left(\dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y \label{2.9}

This says when taking the derivative of an exact differential with respect to the variables, it doesn’t matter what order you do the operations. Later we will prove that ∂w and ∂q are inexact differentials, but first we need to introduce energy.

2.4: Internal Energy (U) and the Equipartition Theorem

As we progress in this course, you will learn that there are four equations for energy. They are the Internal (U), Enthalpy (H), Helmholtz (H) and Gibbs (G) energies. The reason we have four different types of energy is that each is useful under a different set of conditions. To illustrate, if we want to perform a chemical reaction at constant pressure then we must allow the volume of the system's container to change. This is because the reaction might generate a gaseous product, and the pressure would increase if held in a rigid, fixed volume container. As a result, the volume expansion needed to keep pressure constant simultaneously causes a loss of energy due to negative work out of the system. Contrast this to performing the reaction under constant volume conditions, in which there would be no expansion work and thus no loss of energy. This example reveals that the energetics of the reaction are fundamentally different depending on whether it is conducted under constant pressure or constant volume conditions. This in turn requires us to analyze the energy for this chemical process using different equations; this is discussed further in later chapters.

Of the four equations for energy, we will start with the internal energy (U). ***Internal energy is the energy of a single molecule***; this includes the energy that it uses to translate, to rotate and vibrate, and to interact with other molecules. Internal energy is a state function, and its differential ∂U is exact. Since ∂U is exact then there must be an equation for U, and there is: $U = \frac{1}{2} k_B T \cdot (degrees\ of\ freedom)$

where $k_B = \frac{R}{N_A}$, which you can think of as the perfect gas constant for a single molecule. Equation ??? is the Equipartition theorem, which defines internal energy as a function of the molecule's degrees of freedom and temperature. We can determine what are degrees of freedom by logically dissecting what a molecule can "do" and then giving it the thermal energy to do it. We will limit the discussion to gas phase molecules for now to simplify the situation; also, if we discuss the internal energy of a mole of gas molecules then the Equipartition equation is: $U_m = \frac{1}{2} RT \cdot (degrees\ of\ freedom)$, where U_m is the internal energy per mole.

Every atom in every molecule has three degrees of freedom (i.e., ways it can move) because we live in a three-dimensional universe. Furthermore, the number of degrees of freedom for the N atoms adds together; thus, every molecule has a total of 3N degrees of freedom. The Equipartition theorem states that thermal energy flows into and out of these motions equally by an amount $\frac{1}{2} k_B T$. Thus, every molecule ought to have $3N \cdot \frac{1}{2} k_B T$ of internal energy by virtue of the fact it has N atoms at a finite temperature. For example, monatomic argon gas (N=1) has three degrees of translational freedom. Heating a vessel of argon gas causes the atoms to move faster, raising the energy of each individual Ar atom. And if the vessel is cooled, the atoms slow down which lowers their U; in either case the internal energy per mole of argon is $U_m = \frac{3}{2} RT$. The degrees of freedom of an actual molecule like O_2 include rotation and vibration on top of the three translations. Thus, heating a mole of gaseous O_2 results in the molecules translating, rotating, and vibrating more such that there *should be* $3RT$ of internal energy.

However, there is a catch. If $U = 3N \cdot \frac{1}{2} k_B T$ to be true every single degree of freedom must be able to absorb and/or release thermal energy. Experimental measurements demonstrate that the internal energy of a mole of O_2 near room temperature is $\sim \frac{5}{2} RT$, not $3RT$ as expected, which means that one degree of freedom is not contributing to U_m. To discover which one, let's first think about what the degrees of freedom are and then count them. Since we live in a 3-dimensional world, everything has at least three translational degrees of freedom (x, y, and z). For an N-atom molecule, the translational degrees of freedom are for all the atoms moving together in the same direction. Aside translation, the atoms may be moving in such a way that the molecule is rotating. For linear O_2 there are two ways to rotate, one is like a forward flip and the other is a sideways somersault as shown in Figure 2.7. For a non-linear molecule like methane, there are three ways to rotate including the flip, somersault, and a pirouette (Google "pirouette" if you don't know what that is or look at Figure 2.7). Now we need to count the number of vibrations. To do this, we note that all molecules have a total of 3N degrees of freedom. We subtract from this the 3 translations+2 rotations for a linear molecule like O_2, leaving us with 3N-5 vibrations. Consequently, O_2 has one vibrational degree of freedom. Similarly, there are 3N-6 vibrations for non-linear molecules like CH_4.

Concerning O_2, it must be true that the single vibration is not contributing to U_m. To explain, we have to use some quantum mechanics which dictates how molecules vibrate. Quantum mechanics works with an "all or nothing" principle when it comes to changes of energy, meaning that you cannot simply add a small amount of heat to make a bond vibrate a little more. You must add a specific amount of energy (a "quantum") to excite a vibration, and this tends to be much larger than $\frac{1}{2} k_B T$ at room temperature. Thus, vibrations do not *practically* count towards a molecule's internal energy. This is equivalent to stating you cannot "store" heat energy in vibrations. To summarize, Table 1.1 provides a list of molecules, their degrees of freedom, U_m, and the same at terrestrial temperatures where vibrations are "frozen out".

Molecule	Degrees of Freedom	U_m	Terrestrial U_m

	Molecule	Degrees of Freedom	U$_m$	Terrestrial U$_m$	
	Ar	3 translational	3/2 RT12.471 J/mol	3/2 RT12.471 J/mol	
	O_2	3 translational,2 rotational,3$\times$2-5 = 1 vibrational	3 RT24.942 J/mol	5/2 RT20.785 J/mol	
	CO_2	3 translational,2 rotational,3$\times$3-5 = 4 vibrational	9/2 RT37.413 J/mol	5/2 RT20.785 J/mol	
	CH_4	3 translational,3 rotational,3$\times$5-6 = 9 vibrational	15/2 RT62.355 J/mol	3 RT24.942 J/mol	

2.5.1 Internal energy change due to work. As we make progress in our understanding of thermodynamics, we will continuously introduce new thermodynamic variables and ways to calculate their change under various conditions. For example, in the previous section we discussed how to calculate reversible and irreversible work at constant temperature. Now we are requesting you to calculate the changes in U. Fortunately, under isothermal conditions this is incredibly easy because $\Delta U =$ 0 J. This is the result of the fact that, if the temperature doesn't change, nor does the number of atoms in the molecule nor the gas constant (that's a joke fyi), then the U of the gas molecule also doesn't change. This is evident from the differential of the equipartition theorem: $\partial U = \frac{1}{2} k_B \cdot (degrees\ of\ freedom) \cdot \partial T$. Hence, if $\partial T = 0\ K$, then $\partial U = 0\ J$!

We can raise the bar further- what are the heat transactions associated with performing isothermal reversible and irreversible work? First, we must specify that heat is rather narrowly defined as an exchange of energy between the exterior and the system. Furthermore, since $\int \partial U = 0\ J = \Delta w + \Delta q$, then $\Delta q = -\Delta w$. Basically, the change in work energy is counterbalanced by an exchange of heat energy, which is why the temperature doesn't change. This also keeps U constant. Example problem 2.5 below illustrates this and several other principles. It also demonstrates an important point, that being that the individual heat transactions can be added to determine the net heat transaction. This is a manifestation of the 1st law of thermodynamics:

Energy cannot be created nor destroyed

Rather, it just gets shuffled around. Also, the example problem shows that the work resulted in a net release of heat to the environment because Δq is negative. As we will see in Chapter 4, this results in an increase in the entropy of the Universe, which is why we call this process irreversible. And did you notice that the reversible process presented in example problem 2.3 and 2.4 has a $\Delta q_{tot} = \Delta q_1 + \Delta q_2$ = 0 J? This is one reason why we call this process reversible.

2.5: Heat Transactions, Heat Capacity, and Adiabatic Systems

As stated previously, heat (∂q) is narrowly defined as an energy transaction between the exterior and a system. For example, a gas naturally heats up when compressed in a metal piston, which becomes hot to the touch. That is, until it cools through a negative heat transaction (a negative Δq). For a positive Δq the piston will feel cold because the heat is coming out of your hand (the —- exterior) into the system. There is a problem with this definition because it makes it appear that a thermally insulated system magically has no heat at all. This is very incorrect as we shall see in Chapter 4.

Concerning pure heat transactions, any thermodynamic problem must stipulate, “X Joules of energy is added to (or removed from) the system”. Great- what comes next? Taking the viewpoint that heat is added, we know that the temperature increases. Let’s calculate that, and first we must define the relationship between the addition of heat to the increase in temperature ala: $\partial q = ? \cdot \partial T$. Note that there must be some factor “?” in this equation for the simple reason that$partialq$ and$partialT$ do not have the same units. This factor is the heat capacity “C”, which can be defined by modifying the equation above as: $\frac{\partial q}{\partial T} = C$. Note that we have already established that thermodynamic processes can occur at constant volume or constant pressure, which leaves us with two possible definitions for heat capacities, one for constant volume:$frac\partial q\partial T)_V = C_V$ and the other for constant pressure: $frac\partial q\partial T)_P = C_P$. If we know the heat capacities and whether the piston of gas can expand (constant P) or is jammed shut (constant V), we can then calculate a change in temperature by integration: $\frac{\Delta q}{C_{P\ or\ V}} = \Delta T$.

Molecule	$C_{V,m}$ (J/K/mol)	$C_{P,m}$ (J/K/mol)	$C_{P,m}$ - $C_{V,m}$ (J/K/mol)
Ar	12.5	20.79	8.29
O_2	21.1	29.4	8.32
CO_2	28.8	37.1	8.32
CH_4	27.2	35.5	8.32

Shown in Table 2.2 is a list of molecules and their per molar heat capacities. It is important to note that both $C_{V,m}$ and $C_{P,m}$ have units of $J \cdot K^{-1} mol^{-1}$, whereas the true heat capacities C_V and C_P have units of $J \cdot K^{-1}$. Thus, heat capacities are not per molar quantities and are extensive, whereas per molar heat capacities are intensive. We usually present heat capacity in the per molar form in problems and in tables because that information can be generalized. However, you must always remember to multiply the intensive representation of the heat capacity ($C_{V,m}$ or $C_{P,m}$) by the number of moles of your substance to make sure you’re working with the actual heat capacity when addressing thermodynamic problems.

There are a few noticeable trends in Table 2.2, for example, Ar has the lowest heat capacity, and everything has $C_{P,m} > C_{V,m}$. In fact, it appears that the difference $C_{P,m}$ - $C_{V,m}$ is nearly identical to the gas constant R. There must be a physical basis for these observations and for the magnitudes of the heat capacities in general. We will explore heat capacities further by considering what happens when a gas is heated under conditions of constant volume. This is the simplest case because no heat is lost as work, and thus $\Delta U = \Delta w + \Delta q = \Delta q$ since$Deltaw$ = 0 J. The Equipartition theorem states that per molar internal energy: $U_m = \frac{1}{2} RT \cdot (degrees\ of\ freedom)$ can only change with temperature:

$$\partial U_m = \frac{1}{2} R \cdot (degrees\ of\ freedom) \cdot \partial T$$

which leads to:

$$\begin{aligned} C_{V,m} = frac\partial q_m \partial T)_V = \left(\frac{\partial U_m}{\partial T}\right)_V &= \frac{1}{2} R \cdot (degrees\ of\ freedom) \cdot \left(\frac{\partial T}{\partial T}\right)_V \\ &= \frac{1}{2} R \cdot (degrees\ of\ freedom) \end{aligned} \tag{2.5.1}$$

since $\left(\frac{\partial T}{\partial T}\right)_V$ = 1. If you doubt this derivation, check how the numerical values of $C_{V,m}$ in Table 2.2 correlate to the terrestrial U_m in Table 2.1. Overall, it’s a good match. Later we can explain why ”it is that $C_P = C_V + nR$, or equivalently

$C_{P,m} - C_{V,m} = R$. Example problem 2.6 can be used to make sure you understand heat capacities.

2.6.1 Adiabatic Systems. In our exploration of work it was found that compression adds energy into a system. This should cause the gas inside to heat up; however under isothermal conditions a heat transaction with the exterior kept the temperature constant. This heat transaction is expected if the piston is made of metal and is in contact with the exterior. In contrast, example problem 2.6 was used to calculate the increase in temperature after heat energy was added to a gas- why didn't this system cool back down? It's because the piston was wrapped in thermally insulating glass wool. What if we performed compression work on the same insulated piston? For one, Δq must be 0 J because no heat transaction can occur through the thermal insulation. Furthermore, the system can't cool, and the temperature will rise, which results in an increase in ΔU. This is consistent with a positive Δw, which is equal to ΔU since $\Delta U = \Delta w + \Delta q\,(0\ J) = \Delta w$. Of course, we have to give this thermally insulated system it a peculiar-sounding name, and that is "adiabatic". Unfortunately, it has several other definitions sort of like how "bomb" is both a noun and a verb, but for this class an "adiabatic" system is a thermally insulated one.

A system could never be simultaneously both adiabatic and isothermal, as they are opposites. Furthermore, adiabatic processes can be reversible and irreversible just like isothermal transitions. As a result, we now have a total of four paths for thermodynamic processes as summarized here:

Constant temperature, reversible	Adiabatic, reversible
Constant temperature, irreversible	Adiabatic, irreversible

And for each type of transition we can calculate five variables: ΔU, Δq, Δw, C_V, and C_P. Let me correct that- we have five variables *for now*. We are going to end up with 12 by Chapter 5, times the four types of transitions, gives us 4×12 = 48 potential thermodynamic relationships!

2.6.1.1 Adiabatic, Reversible. We must consider how work changes the temperature of an adiabatic system. In fact, for all adiabatic processes the first thing we must calculate is the final temperature, since the initial temperature must be known. Normally, it would appear that we should be able to determine the final temperature using an equation of state such as the perfect gas law. However, the perfect gas law won't help us with adiabatic transitions because PV=nRT is just one equation with three variables changing simultaneously (P, V, and T). Another approach is required, such as calculating all the energy imparted via work and then use the heat capacity to translate that energy into ΔT. Let's use ∂U as a conduit to realize this approach. First, $\partial U = \partial w + \partial q = \partial w$ as ∂q ***is always 0 J*** under adiabatic conditions. Next, as ∂U is exact it can be calculated either reversibly or irreversibly and we will get the same answer. Generally, it is easier to use the reversible path, which makes $\partial U = \partial w = -P\partial V$.

To connect $\partial U = -P\partial V$ to the change in temperature we will use the example of an adiabatic expansion shown in Figure 2.8. In this process, the volume increases with a simultaneous decrease in temperature. So how do we account for both volume and temperature change when calculating the effect on internal energy? Due to the "exactness" of ∂U we can decouple these processes into different routes with the same start and end points. For example, the system can follow path 1 where there is a change in volume at a fixed temperature; as a result there is no change in internal energy ($\Delta U_1 = 0\ J$). Path 2 represents a temperature change at constant volume, which makes $\Delta U_2 = C_V \Delta T$ and thus $\Delta U_{tot} = \Delta U_1 + \Delta U_2 = C\,_V \Delta T$. We can also determine the same following the alternative route Path 3 + Path 4, which simply follow the reverse order yet have the same change in total U. Ultimately, $\Delta U_{tot} = C_V \Delta T$ regardless of the route followed, and this is equal to the work as discussed previously. We will switch to partial notation so that we can apply integral calculus on relationship:

$$C_V \partial T = -P\partial V \tag{2.5.2}$$

The remainder of the proof will rely on perfect gas conditions, i.e. $PV = nRT$ and thus $P = \frac{nRT}{V}$ which we plug into Equation 2.12:

$$C_V \partial T = -\frac{nRT}{V}\partial V$$

This is important because we must integrate with respect to T and V (the partials in Equation 2.12), and thus we must make sure the T and V that were "hiding" in P are now on the left and right sides. The integral limits (final minus initial) are T_f to T_i on the left and V_f to V_i on the right:

$$\int_{T_i}^{T_f} \frac{C_V}{T}\partial T = -\int_{V_i}^{V_f} \frac{nR}{V}\partial V$$

After integration we find:

$$C_V \cdot \ln\left(\frac{T_f}{T_i}\right) = -nR \cdot \ln\left(\frac{V_f}{V_i}\right)$$

Now we can apply several identities for natural logs, such as: $-\ln\left(\frac{a}{b}\right) = \ln\left(\frac{b}{a}\right)$, as well as:

$a \cdot \ln(b) = \ln(b^a)$ to make the following rearrangements:

$$\frac{C_V}{nR} \cdot \ln\left(\frac{T_f}{T_i}\right) = \ln\left(\frac{V_i}{V_f}\right)$$

and thus: $\ln\left[\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}}\right] = \ln\left(\frac{V_i}{V_f}\right)$

""""Taking the exponential of both sides results in:

$$\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f} \tag{2.5.3}$$

which gives a method for calculating the final temperature of a reversible adiabatic process. Basically, any question on adiabatic transitions will provide all the necessary information for calculating T_f via $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ or a derivative thereof, albeit the data may be obscured using the perfect gas law. Another interesting aspect of $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$, which we sometimes refer to as an "" "adiabatic equation of state", is that it appears to be an alternative for the perfect gas law. However, this is incorrect as we used PV=nRT in the derivation of this equation, and we can use PV=nRT to make further derivations of $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ which is on several problems at the end of the chapter.

To summarize and provide some problem-solving strategies, a reversible adiabatic

transition has = 0 J, and the next step is to determine ΔT via T_f. Next, the change in U is $C_V \Delta T$, which is also the work. Hopefully example problems 2.7 and 2.8 will solidify the lessons learned.

2.6.1.2 Adiabatic, Irreversible. Irreversible adiabatic work appears to be much simpler compared to the reversible, as the work is against a constant exterior pressure. As a result, $\partial w = -P_{ext} \partial V$, and as it is still true that $\partial U = \partial w = C_V \partial T$, integration yields:

$$C_V \Delta T = -P_{ext} \Delta V \tag{2.5.4}$$

Doesn't it look much easier to calculate the irreversible ΔT compared to the reversible example above? Of course, and as you can imagine that is very wrong. Example problem 2.8 will help you navigate irreversible, adiabatic equations for work.

Note that the example problem demonstrates less negative work (-621 J) than observed in the reversible problem (-828 J); this preserves the notion that we get the most (negative) work out of reversible transitions. And how did that extra work come about? It's because the reversible expansion ends up with a much colder gas, which means more internal heat was converted to expansion work. Think of it like this: if the change in temperature was calculated from $\Delta w = n \cdot C_{V,m} \cdot \Delta T$, then $\Delta T = \frac{\Delta w}{n \cdot C_{V,m}}$. Now since the reversible work is the most negative, then the reversible transition will cool the gas more compared to the irreversible transition.

Conclusion. Thus far we have shown the basics of energy, heat and work, via the 1^{st} Law of Thermodynamics. However, we still have much to learn before analyzing chemical processes; in fact, the content of this chapter uses gas expansion and contraction in place of chemical transformations because understanding a car engine piston is much easier than burning gasoline. This will be the case until you reach Chapter 6, but for now we move on to understanding other types of energy and how they apply to the four thermodynamic transformational conditions.

CHAPTER OVERVIEW

3: Enthalpy, Legendre Transforms, and Thermodynamic Proofs

In the previous chapter you learned about a molecule's internal energy (U) and how it is defined from the Equipartition theorem. However, there are three more types of energy, each of which is applicable depending on the nature of the system and transition under study. For example, the change in internal energy (U) is equal to heat exchange under conditions of constant volume because no PV work can be done. Thus, U does not describe heat exchange in systems where the pressure is held constant, whereas another definition of energy called the Enthalpy serves this role. This chapter begins by further studying heat, which is important because electricity is generated by burning fuel that turn the turbines, rather than from work using a team of donkeys. At least, ***not now***.

3.1: Enthalpy and Changing Functions

Internal energy is not as important in constant pressure (i.e. volume-changing) systems due to the fact that some work energy is in play. As a result, some of the system's energy is gained or lost by the contraction or expansion of the vessel that the gas is in. As a result, we should define another type of energy that is more useful for describing constant pressure systems, which we will call enthalpy (H):

$$H = U + PV \tag{3.1.1}$$

One simple description of enthalpy is that it accounts for the ability to do work as represented by the addition of PV in Equation 3.1, which has units of Joules. As in all things, we are not concerned with thermodynamic variables but changes in those variables during dynamic processes. This prompts us to review the mathematics of change, which are calculus derivatives. The change in P times V prompts the use of the product rule defined as:

$$\frac{\partial\left(f\left(x\right)\cdot g\left(x\right)\right)}{\partial x} = f\left(x\right)\frac{\partial g\left(x\right)}{\partial x} + g\left(x\right)\frac{\partial f\left(x\right)}{\partial x} \tag{3.1.2}$$

We will use the following symbology to describe Equation 3.2, which is common in multivariable calculus:

$$\partial\left(f\cdot g\right) = f\cdot\partial g + g\cdot\partial f \tag{3.1.3}$$

When Equation 3.3 is applied to our new function enthalpy we find:

$$\partial H = \partial U + \partial\left(P\cdot V\right) = \partial U + V\partial P + P\partial V \tag{3.1.4}$$

Since we are concerned with constant pressure systems, meaning $\partial P = 0\ Pa$:

$$\partial H = \partial U + P\partial V \tag{3.1.5}$$

This relationship reveals the utility of enthalpy. First, since U is a state function we can calculate the change in U, i.e. $\partial U = \partial q + \partial w$, any way we want. As such, we will use the reversible path which means $\partial w = -P\partial V$ and as a result: $\partial U = \partial q - P\partial V$. We find after inserting this expression into Equation 3.5:$\partial H = \partial q - P\partial V + P\partial V = \partial q$

Enthalpy is heat! In fact, you probably already knew this, because in Freshman Chemistry we told you that the difference in endothermic and exothermic processes depends on a positive or negative ΔH. Did you just say "Ah-ha I always knew that enthalpy was the heat of a reaction!"? But didn't you learn the same thing about internal energy in the previous chapter? Isn't it true that endo/exothermic is determined by U so long as volume is constant? It is- this is not a trick question- the heat of a reaction is the change of internal energy at constant V, while heat is the change in enthalpy when at constant P.

So, you might feel that you have been lied to, which, you have. But why? To answer, go outside and look up. Do you see a metal box containing the entire planet's atmosphere at a constant volume? No? Then the Earth is a constant pressure system. Now think back to your lab courses. How often was it true that you set up a reaction in a fully enclosed vessel? Note a Schlenk line found in a real research lab aren't enclosed- they have valves that relieve a buildup of pressure for safety's sake. This brings us to our point, which is that it is very rare for chemical processes to be performed at constant volume. Nature doesn't do it, and chemists who care about life and limb also don't do it. Thus, in your earlier learnings about thermodynamics, we stated that endo/exothermicity is due to enthalpy because that is generally true. But not always.

3.1.1 Calculating Enthalpy

Regardless of whether we are studying isothermal or adiabatic processes at constant pressure or volume, you can always calculate the change in enthalpy from Equation 3.4: $\partial H = \partial U + \partial\left(P\cdot V\right)$. First, let's tackle isothermal transitions, both reversible and irreversible. Starting with ∂U, we already learned that $\partial U = 0\ J$ at constant T because of the Equipartition theorem; internal energy can only change if temperature changes. Oddly, this is consistent with the adiabatic formula for changing internal energy: $\partial U = C_V\partial T$, which is likewise $0\ J$ under isothermal conditions ($\partial T = 0\ K$). The formula $\partial U = C_V\partial T$ works for both isothermal and adiabatic transitions because ∂U is an exact differential, and as a result we can simplify our formula for changing enthalpy: $\partial H = C_V\partial T + \partial\left(P\cdot V\right)$. Next, we must figure out what to do with the $\partial\left(P\cdot V\right)$ term, which is a bit complex because both P and V may be simultaneously changing for some situations. However, there is an easy way to resolve this; given that we are presently focused on gases we can use the perfect gas law to find:

$$\partial\left(P\cdot V\right) = nR\partial T \tag{3.1.6}$$

which is true because we assume both n (moles) and R (=8.314 J/K/mol) are constants. This leaves us with:

$$\partial H = C_V \partial T + nR\partial T = (C_V + nR)\,\partial T \tag{3.1.7}$$

We will use Equation 3.6 for many problems, and as it applies here it shows that $\partial H = 0\ J$ for isothermal processes regardless of whether the path is reversible or irreversible.

Under adiabatic conditions there is thermal insulation covering the reactor vessel or piston, which means heat or work results in a temperature change. Thus, to calculate the change in enthalpy for adiabatic changes one first determines the change in temperature ΔT from Equation 2.14 (reversible) or Equation 2.15 (irreversible) and use that result into the integrated form of Equation 3.7: $\Delta H = (C_V + nR)\,\Delta T$. This will also apply to both reversible and irreversible adiabatic transitions since ∂H is exact. As we pointed out in Ch. 2 that $C_P = \ C_V + nR$, which we will prove rigorously below, it is also true that $\Delta H = C_P \Delta T$

3.1.2 Proofs. Up or down?

The purpose of thermodynamic proofs is to determine relationships between variables that are not immediately obvious. For example, does internal energy (U) rise or fall with increasing volume under adiabatic conditions (i.e. $\partial q = 0\ J$)? This is such a specific question I cannot instinctually answer. However, if we do a formal derivation then we can figure this out. Starting with:

$$\partial U = \partial w + \partial q = -P\partial V$$

we can divide by the change in volume and hold the heat (q) constant:

$$\left(\frac{\partial U}{\partial V}\right)_q = -P\left(\frac{\partial V}{\partial V}\right)_q = -P$$

where we used the fact that $\left(\frac{\partial V}{\partial V}\right)_q = 1$. As pressure is always positive, $-P$ is always negative, and thus internal energy always decreases with increasing volume under adiabatic conditions. Note that we designate heat (q) as constant in the partial derivatives, i.e. $\left(\frac{\partial U}{\partial V}\right)_q$ and $\left(\frac{\partial V}{\partial V}\right)_q$, thus, it isn't "just P or V that can be held constant in thermodynamic proofs. We can hold anything we want constant.

Hopefully you see the value of thermodynamic proofs, after all how else could you have answered this question? However, perhaps this is more obvious than you realized given what you know about adiabatic transitions. Since a piston is thermally insulated, and volume increases, then the temperature will decrease. Don't your instincts tell you that a gas cools upon expansion? And since you know that decreasing the temperature will decrease the internal energy according to the Equipartition theorem, then it makes sense that $\left(\frac{\partial U}{\partial V}\right)_q$ is negative! Example problems 3.1 and 3.2 are provided to give you some more practice with proofs.

You may have noticed that work, $\partial w = -P_{ext}\partial V$, is always assumed to be reversible: $\partial w = -P\partial V$ in just about every example of calculating or deriving ∂U or ∂H. This is because these energies are state functions, and their differentials are exact and path independent. As a result, we can always use reversible work in these derivations, which makes the effort significantly simpler. We don't have to use irreversible work, even if the process under scrutiny is irreversible, since we would still determine the same ∂U or ∂H. Using the irreversible definition is tantamount to intentionally make these derivations more complex.**3.2 Heat Capacities. 3.3 Natural Variables and Legendre Transforms. 3.4 The Joule and Joule-Thomson Experiments.** Back in early 1800's, Sir James Joule was a somewhat well-off brewer who became interested in using mechanical means to produce heat. The problem was that no one thought that work could become heat, despite the fact that this is incredibly obvious to anyone who rubs their hands together in the cold. Joule was able to perform fairly sophisticated measurements to show that work does indeed transform to heat, sometimes using contraptions nearly the size of a house. Ultimately, Joule's efforts led to the 1^{st} Law of Thermodynamics.

Part of Joule's research centered on testing thermodynamic theories, especially concerning work and heat. For example- we all know that an expanding gas gets cold. Or does it? First, imagine a thermally insulated system (i.e. adiabatic, so $\partial q\ = 0\ J$ which should be a knee-jerk reaction for you when “adiabatic” is stipulated). Inside of this device is a pressurized container connected with a valve to another vessel under vacuum; this is shown in Figure 3.1. If the gas cools when the valve opens and the gas expands into the vacuum, then there should be a decrease in the surrounding water temperature as measured by the thermometer. Of course, our instincts tell us that the expanding gas will cool, and the water will chill.

Joule did this experiment and oddly the water temperature didn't change at all! However, later the experiment was repeated with better equipment and it was found that the water bath did cool, just not very much. And it gets more interesting- if you use hydrogen or helium, the water *gets slightly warmer*. It seems that this system is much more complicated than originally though! To delve deeper, we need to determine how temperature changes when a gas increases its volume: $\left(\frac{\partial T}{\partial V}\right)_?$, but it isn't clear what variable is held constant in the Joule contraption. We can figure this out in several steps, first noting that the gas expands into a vacuum ($P_{ext} = 0\ Pa$). As a result, the work of expansion is $\partial w = -P_{ext}\partial V = 0\ J$. And $\partial q = 0\ J$ due to the adiabatic conditions, which makes $\partial U = \partial w + \partial q = 0\ J$; thus the expansion occurs under conditions of constant internal energy. Consequently, the Joule experiment measures the change in volume under constant internal energy conditions, i.e. $\left(\frac{\partial T}{\partial V}\right)_U$. Now we will use a math identity called the Euler Chain formula, Equation 3.11, which is derived on the previous page if you're interested. We will start with:

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x$$

and apply it to $\left(\frac{\partial T}{\partial V}\right)_U$, where $x = T$, $y = V$ and $z = U$: $\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T$. Recall that $\partial U = C_V\partial T$ and thus $\frac{1}{C_V} = \left(\frac{\partial T}{\partial U}\right)_V$, which allows us to summarize:

$$\mu_J = \frac{\partial T}{\partial V})_U = -\frac{1}{C_V}\cdot\left(\frac{\partial U}{\partial V}\right)_T \tag{3.1.8}$$

where μ_J is called the Joule coefficient.

Now we see why the Joule experiment is so odd. Since it is setup such that $\partial U = 0\ J$, then there should be no change in temperature because $\partial U = C_V\partial T$. The Joule coefficient (μ_J) likewise should be $\sim$0 K/m^3 since it is equal to $\left(\frac{\partial T}{\partial V}\right)_U$ and we expect $\partial T = 0\ K$. However, note that we stated that the change in temperature was not *exactly* zero, it was only *close* to 0 K. This behavior can be understood when we view the Joule coefficient as $\mu_J = -\frac{1}{C_V}\cdot\left(\frac{\partial U}{\partial V}\right)_T$. By the end of Chapter 4 you will be able to do a thermodynamic proof to show that $\left(\frac{\partial U}{\partial V}\right)_T = 0\ J/m^3$ for a perfect gas, but $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ for a van der Waals gas. Consequently, the non-zero Joule coefficient is due to real gas behavior. For example, a real gas differs from a perfect gas because the real gas molecules interact, and now we see that this affects the internal energy. Most gas molecules have energy-lowering self-interactions via the attractive ‘‘a'' parameter as explained in Chapter 1, which means that getting closer as the volume decreases $(\partial V < 0\ m^3)$ lowers the energy$(\partial U < 0\ J)$, resulting in a positive $\left(\frac{\partial U}{\partial V}\right)_T$ which is consistent with from $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ the van der Waals equation. Thus, expanding the gas cools it, just very slightly. However, hydrogen and helium are oddballs- they have very small self interactions and higher compressibility factors. As a result, these gases get warmer when expanded in a Joule apparatus.

3.2: Heat Capacities

At this point we have enough thermodynamic variables to derive more complex relationships. For example, we have shown that $\partial H = \partial q$ at constant pressure. Since $\partial q = C_P \partial T$ at constant P, then $\partial H = C_P \partial T$ which allows us to define heat capacity at constant pressure as $C_P = \left(\frac{\partial H}{\partial T}\right)_P$. We have also shown above that $\partial H = (C_V + nR)\,\partial T$, which must mean that the two forms of heat capacity are related via $C_P = C_V + nR$, which is consistent with the data in Table 2.2 of Chapter 2. Here we present an exact proof of this relationship. In fact, there are two derivational routes to do so, and both are shown. It is also instructive to see that there are multiple methods to demonstrate thermodynamic relationships.

Method 1: We have already shown that $\partial U = \partial w + \partial q = -P\partial V + \partial q$, which is due to the exactness of internal energy. If we bring ∂q to the left side of the equation:

$$\partial q = C_V \partial T + P \partial V$$

and divide by ∂T: $\frac{\partial q}{\partial T} = C_V \frac{\partial T}{\partial T} + P \frac{\partial V}{\partial T}$, and then keep P constant:

$$\left(\frac{\partial q}{\partial T}\right)_P = C_P = C_V \left(\frac{\partial T}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P$$

Clearly $\left(\frac{\partial T}{\partial T}\right)_P = 1$ and $P\left(\frac{\partial V}{\partial T}\right)_P = P\left(\frac{\partial \frac{nRT}{P}}{\partial T}\right)_P = P\frac{nR}{P} = nR$. Thus, $C_P = C_V + nR$.

Method 2: This derivation is unfortunately more complex. Starting with:

$$\partial H = \partial U + \partial (PV) = \partial U + V\partial P + P\partial V$$

we divide by ∂T:

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + V\frac{\partial P}{\partial T} + P\frac{\partial V}{\partial T}$$

Note that we haven't made anything constant yet. We can set anything we want to be constant, but we should choose something that makes sense like pressure:

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

Since $\left(\frac{\partial H}{\partial T}\right)_P = C_P$ by definition and $V\left(\frac{\partial P}{\partial T}\right)_P = 0 fracm^3PaK$ since $\partial P = 0\ Pa$ at constant pressure:

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

Using the perfect gas law: $P\frac{\partial V}{\partial T})_P = P\frac{\partial \frac{nRT}{P}}{\partial T})_P = P\frac{nR}{P} = nR$, leaving us with:

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + nR$$

We are so close to proving $C_P = C_V + nR$, but we can't just state $\left(\frac{\partial U}{\partial T}\right)_P = C_V$ out of thin air (but we can already see $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V = C_V$ must be true!). Let's show this with another proof by deriving ∂U with changing T and V:

$$\partial U = \left(\frac{\partial U}{\partial T}\right)_V \partial T + \left(\frac{\partial U}{\partial V}\right)_T \partial V$$

(recall that this is the proper form for the change of a multivariable function, Equation 2.7). Next, we divide by ∂T:

$$\frac{\partial U}{\partial T}=\left(\frac{\partial U}{\partial T}\right)_V\frac{\partial T}{\partial T}+\left(\frac{\partial U}{\partial V}\right)_T\frac{\partial V}{\partial T}$$

Setting pressure constant moves things along nicely:

$$\left(\frac{\partial U}{\partial T}\right)_P=\left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial T}\right)_P+\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

And now we can make several simplifications. For one, $\left(\frac{\partial T}{\partial T}\right)_P=1$, $\left(\frac{\partial U}{\partial T}\right)_V=C_V$ (by definition), and $\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P=0\ J/K$ because $\left(\frac{\partial U}{\partial V}\right)_T=0\ J/m^3$. Why is that? Because we can infer $\partial U=0\ J$ since T is constant; as always, there is no change in internal energy at constant temperature due to the Equipartition theorem. We are left with: $\left(\frac{\partial U}{\partial T}\right)_P=\left(\frac{\partial U}{\partial T}\right)_V=C_V$, and going back to: $C_P=\left(\frac{\partial U}{\partial T}\right)_P+nR$, we can finally finish the proof:

$$C_P=C_V+nR \tag{3.2.1}$$

To summarize, we have defined a new type of energy, called enthalpy, via $H=U+PV$. The change in enthalpy is the heat exchange under constant pressure conditions. Enthalpy also provides a definition for C$_P$ and explains why the heat capacity is highest under constant pressure conditions. Overall, it appears that there is a special relationship between pressure and enthalpy, just as we saw with volume and internal energy. The next section will shed light on this fact.

3.3: Natural Variables and Legendre Transforms

It is more than just happenstance that $\partial U = \partial q$ and $\partial H = \partial q$ at constant V and P, respectively. To understand more of the fundamentals we introduce here the concept of “natural variables” in thermodynamics. Natural variables are revealed when we examine how thermodynamic variables change, i.e. we derive their differentials. For example, in an adiabatic system $\partial U = \partial w = -P\partial V$, and we see that the expression relates ∂U to ∂V *but not* ∂P. This makes internal energy U connected with volume in a fundamental way that it is not with pressure; as a result, we state that V is a natural variable of U. Note that when U’s natural variable volume is held constant, then an important relationship emerges, which is that $\partial U = \partial q$ (i.e. the change in internal energy is the heat transaction).

Here we formalize the definition of a natural variable using calculus. Recall that the change of a function $f\left(x\right)$ is:

$$\partial f\left(x\right) = \frac{\partial f}{\partial x}\partial x \tag{3.3.1}$$

We say that x is the natural variable of function f, and $\frac{\partial f}{\partial x}$ is the conjugate of x. Let’s define a new function called g using f, x, and x’s conjugate:

$$g = f - \left(\frac{\partial f}{\partial x}\right)\cdot x \tag{3.3.2}$$

What is the natural variable of g? To find out, we must determine ∂g and see what makes it change; note the use of the product rule and the color coding to help you see how equations 3.9 and 3.10 are combined:

$$\partial g = \partial f - \partial\left\{\left(\frac{\partial f}{\partial x}\right)\cdot x\right\} = \frac{\partial f}{\partial x}\partial x - \frac{\partial f}{\partial x}\cdot\partial x - x\cdot\partial\left(\frac{\partial f}{\partial x}\right) = -x\cdot\partial\left(\frac{\partial f}{\partial x}\right)$$

Thus $\partial g = -x\cdot\partial\left(\frac{\partial f}{\partial x}\right)$, and we conclude that $\left(\frac{\partial f}{\partial x}\right)$ is the natural variable of function g. To summarize, what we did was take a function and subtract its natural variable times the natural variable’s conjugate. This is called a Legendre transform, and it takes an old function with a natural variable and creates a new function with a different natural variable (that being the conjugate of the old natural variable).

You might be asking, in the example above how can the derivative $\left(\frac{\partial f}{\partial x}\right)$ also be variable? Also, is the partial of a derivative $\partial\left(\frac{\partial f}{\partial x}\right)$ meaningful, or is it mathematical gibberish? To address this, let’s examine a function like internal energy under adiabatic, reversible conditions: $\partial U = -P\partial V$. To equate this to $\partial f\left(x\right) = \frac{\partial f}{\partial x}\partial x$, we see that $U = f\left(x\right)$ and $V = x$, then we can also see that: $\partial U = \frac{\partial U}{\partial V}\partial V = -P\partial V$ which means $\frac{\partial U}{\partial V} = -P$. Thus, negative pressure is conjugate to internal energy’s natural variable volume.

Let’s now explore the use of a Legendre transform on U, whereby we create a new function that has a natural variable of pressure. Starting with the definition of a Legendre transform, Equation 3.10: $g = f - \left(\frac{\partial f}{\partial x}\right)\cdot x$, we recognize that $f\left(x\right) = U$, $x = V$, and $\frac{\partial f}{\partial x} = -P$:

$$g = U - \left(\frac{\partial U}{\partial V}\right)\cdot V = U - \left(-P\right)V = U + PV$$

And now we see that this Legendre transform of U is the enthalpy H. To determine enthalpy’s natural variables, we differentiate it under adiabatic conditions:

$$\partial H = \partial U + \partial\left(PV\right) = -P\partial V + P\partial V + V\partial P = V\partial P$$

Hence pressure is a natural variable of H, and $\frac{\partial H}{\partial P} = V$ is conjugate to pressure. Although we have performed this derivation by invoking adiabatic reversible conditions, it is true that $H = U + PV$ for any transition since U and H are state variables.

3.3.1 Inexactness of q. As all this talk of natural variables and conjugates may be overwhelming and too abstract, we will slow down and work an example to solidify your understanding. Recall in Chapter 2 we were able to demonstrate that work $\left(\partial w\right)$ is inexact due to the fact that reversible and irreversible work are not the same. Here we show that heat $\left(\partial q\right)$ is also inexact, facilitated by the fact that we know more about heat capacity and have had a lot of practice with partials. First, we start with the familiar relation: $\partial U = \partial$��$+ \partial w$, and following the reversible path $\left(-\partial w = P\partial V\right)$ means $\partial q = \partial U - \partial w = \partial U + P\partial V$. Next we substitute$partial U = C_V\partial T$, and as a result $\partial q = C_V\partial T + P\partial V$. Now we need to make sure that we understand what our function is, what are the natural variables and those variables’ conjugates. We do so by lining up ∂q above with the expression for the change in a function $\partial f\left(x,y\right) = \left(\frac{\partial f}{\partial x}\right)_y\partial x + \left(\frac{\partial f}{\partial y}\right)_x\partial y$ as follows:

It is clear that f=q, x=T, and y=V, and $\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial q}{\partial T}\right)_V = C_V$ and $\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial q}{\partial V}\right)_T = P$. Let us now define what it means to be inexact using Equation 2.9, the Euler test (an inexact partial fails the Euler test, hence the $\neq$):

`\left( \dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x\neq \left( \dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y \nonumber`

Making the proper substitutions defined above yields:

`\left( \dfrac{\partial }{\partial V}{\frac{\partial q}{\partial T} \right)_V)}_T\neq \left( \dfrac{\partial }{\partial T}{\frac{\partial q}{\partial V} \right)_T)}_V \nonumber`

The right-hand double derivative is: `\left( \dfrac{\partial }{\partial T}{\frac{\partial q}{\partial V} \right)_T)}_V=\left( \dfrac{\partial P}{\partial T} \right)_V`. We assume perfect gas conditions, i.e. $P = \frac{nRT}{V}$, leaving us with: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial nRT/V}{\partial T} = \frac{nR}{V}$. The left-hand side is: `\left( \dfrac{\partial }{\partial V}{\frac{\partial q}{\partial T} \right)_V)}_T=\left( \dfrac{\partial C_V}{\partial V} \right)_T` since $\partial q = C_V\partial T$. Unfortunately, $\left(\frac{\partial C_V}{\partial V}\right)_T$ requires some effort. Recall that the heat capacity at constant volume is related to the internal energy via: $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{2}nR\cdot\left(degrees\ of\ freedom\right)$ as we demonstrated in Chapter 2, Equation 2.11. There is no volume dependence to the degrees of freedom, at least for a perfect gas since they don’t interact with each other. As a result, there is no reason to believe that there is any volume dependence to the heat capacity, which makes the derivative with respect to volume $\left(\frac{\partial C_V}{\partial V}\right)_T = 0\ J/m^3$. Thus, heat is not exact because it fails the Euler test:

`\left( \dfrac{\partial }{\partial V}{\frac{\partial q}{\partial T} \right)_V)}_T=0\ J/m^3\neq {\frac{nR}{V}=\frac{\partial }{\partial T}\left( \dfrac{\partial q}{\partial V} \right)_T)}_V \nonumber`

3.4: The Joule and Joule-Thomson Experiments

Joule was buddies with Lord Kelvin, or William Thomson as he was known at the time. At first Thomson believed in the “caloric” theory of heat, which is that heat is like mass and can transfer between objects. However, at a scientific conference Joule was able to convince Thomson that heat and work were transferrable, and they set out to test this hypothesis using a different contraption whereby gas was pushed from one vessel through a “throttle” into another. The Joule-Thomson device is shown in Figure 3.2. There are two tricks to this experiment. One is that all the gas is transferred, meaning that all thermodynamic variables are 0 initially for the right side of the container and are 0 in the final state for the left container. This is because no gas has no volume and no energy. The other clever move is that the “throttle” in between the left and right sides allows the gas to be transferred such that the compression on the left and expansion on the right occur at constant pressure.

Let us slow down and analyze the Joule-Thomson experiment in steps. Initially, all the gas is on the left side and has an internal energy of U_1; we will say that the gas is in “state 1”. All the gas is transferred to the right side of the device in state 2, so the final internal energy is U_2. Mathematically all of this is expressed as:

$$\Delta U = \int_{U_1}^{U_2} \partial U = U_2 - U_1$$

The system is adiabatic ($\partial q = 0$ J), which means that the changes in internal energies are entirely due to work. Thus, for both vessels, $\Delta U = \int \partial w$. The total work is the sum of that performed on the left and right sides. The left-side work is easy to calculate because the pressure of the 1^{st} vessel is constant as the plunger is compressed, resulting in:

$$\Delta w_1 = -\int_{V_1}^{0\ L} P_1 \cdot \partial V = -P_1 \cdot (0\ L - V_1) = P_1 V_1$$

Likewise, the work on the right side is:

$$\Delta w_2 = -\int_{0\ L}^{V_2} P_2 \cdot \partial V = -P_2 \cdot (V_2 - 0\ L) = -P_2 V_2$$

and the total work is $P_1V_1 - P_2V_2$. We can now equate the change in internal energy with the total work:

$$U_2 - U_1 = P_1V_1 - P_2V_2$$

thus, $U_2 + P_2V_2 = U_1 + P_1V_1$ or $H_2 = H_1$, resulting in $\Delta H = 0\ J$. Consequently, the Joule-Thomson experiment is isoenthalpic.

As with the Joule experiment, you are probably questioning whether the gas gets hot or cold in the process. Similar to the previous example we will apply $\left(\frac{\partial T}{\partial P}\right)_H$ to the Euler chain: $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$ to determine the Joule-Thomson coefficient:

$$\mu_{J-T} = \left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \tag{3.4.1}$$

using the fact that $\left(\frac{\partial T}{\partial H}\right)_P = \frac{1}{C_P}$. Similar to Joule’s experiment, if $\partial H = 0\ J$ then the transition should be isothermal, i.e. $\partial T = 0\ K$. However, depressurizing a gas generally results in a modest cooling which must be due to real gas behavior. The cooling of a gas is much easier under isoenthaplic conditions, and as a result the Joule-Thomson experiment led to modern refrigeration. Shown in Table 3.0 are various Joule-Thomson coefficients, where we can see that most gases have positive coefficients which means that the gas will cool upon depressurization. The effect is rather large for ammonium and Freon, and as before we see that hydrogen is an outlier. Because of ammonia’s large positive μ_{J-T} the first refrigeration plants used ammonium as a coolant, which was as bad an idea because they tended to explode. People then turned to the use of Freon, also known as R22 which is a mixture of chlorofluorocarbons, which was also a bad idea because it destroyed the ozone layer. This is why we use R410A now, which is better than ammonia or Freon; however, it is a powerful greenhouse gas.

	Gas	μ_{J-T} (K atm^{-1})
	Helium	-0.062

	Gas	μ_{J-T} (K atm^{-1})	
	air	0.227	
	CO$_2$	1.11	
	Freon	1.20	
	NH$_3$	3.39	

As part of the Chapter 5 homework problems you will demonstrate that $\left(\frac{\partial H}{\partial P}\right)_T = 0\ J/Pa$ for a perfect gas, while $\left(\frac{\partial H}{\partial P}\right)_T \approx nb - \frac{2na}{RT}$ for a real (van der Waals) gas. To do these derivations you have to learn about entropy and the 2^{nd} Law of Thermodynamics. This also gives you the tools to explore much further advanced thermodynamic derivations.

Conclusion. This chapter has shown you how new equations for energy can be defined by the Legendre Transform. Specifically, Enthalpy was introduced by a simple manipulation of Internal energy, and it has utility when a transformation is performed under constant pressure conditions. But what if temperature isn't constant? As we move forward, we will study changes in temperature and make further use of the Legendre Transform. Of course, we must know what thermodynamic variable is the conjugate of temperature. That just happens to be entropy.

CHAPTER OVERVIEW

4: Entropy and the 2nd Law

This chapter introduces entropy, which is the most important thing in the Universe (even more than a cell phone, which does nothing but create entropy anyways). You might be familiar with entropy as the “buildings fall down” principle; however you have to add in “nothing works perfectly” to fully described the 2^{nd} Law of Thermodynamics. The latter probably explains all the events of your life. In fact, the 2^{nd} Law is so important, the 3^{rd} Law of Thermodynamics’ purpose is mostly to validate it by providing an entropy yardstick.

4.1: Introduction to Entropy

There are several ways to describe entropy. For example, word on the street is that entropy is the amount of randomness of a system. True, but let's add some nuances- entropy is randomness of a system *as created by heat*. Here is another description- the entropy of a material affects how heat changes it, like how the solubility of a salt in water dictates the solution's salinity. These descriptions are consistent with a change of entropy loosely defined as $\partial S=\frac{\partial q}{T}$, or $\Delta S=\frac{\Delta q}{T}$ if integrated. Let's apply this to situations that create "randomness" at a constant temperature such as a phase change. In this regard, it should be obvious that boiling water generates more entropy than melting ice. Consequently, if $\Delta S=\frac{\Delta q}{T}$ is true then it must also be the case that:

$$\frac{\Delta q_{vap}}{T_{vap}}\gg\frac{\Delta q_{melt}}{T_{melt}}$$

Water vaporization requires a lot of heat (Δq_{vap} = +41.7 kJ/mol) at a moderately high temperature (T_{vap} = 373 K). Melting ice occurs at a lower temperature (T_{melt} = 273 K) but doesn't require nearly as much heat (Δq_{melt} = +6.0 kJ/mol). Consequently:

$$\frac{\Delta q_{vap}}{T_{vap}}=112\ J/K\gg 22\ J/K=\frac{\Delta q_{melt}}{T_{melt}}$$

Thus, Equation 4.1.1 for entropy makes sense.

As further proof, we contend that the entropy of vaporization: $\Delta_{vap}S=S_{gas,m}-S_{liq,m}$, ought to be nearly the same for most chemical substances. This is because gases have a very high entropy while liquids have significantly less. Furthermore, gases have very similar behavior as revealed by the near universality of the perfect gas law (meaning that PV=nRT works regardless of the gas's chemical identity). As a result, the difference between the entropy of a gas and liquid ($\Delta_{vap}S$) should likewise be nearly universal. Shown in Figure 4.1 is the enthalpy of vaporization $\Delta_{vap}H_m$, which is the heat exchange (Δq_{vap}) necessary to boil a substance at constant pressure, versus the boiling (vaporization) temperature T_{vap} for $\sim$100 chemicals. If our definition of the change of entropy is correct: $\Delta_{vap}S_m=\frac{\Delta_{vap}H_m}{T_{vap}}$, then we expect linear behavior between the heat and temperature via:

$$\Delta_{vap}H_m=\Delta_{vap}S_m\times T_{vap}$$

Clearly Figure 4.1 is a line with a slope of $\sim$10.5 R, something that was noted back in 1884 by Frederick Trouton, an undergraduate student in Trinity College. Today we state that the entropy of vaporization of most chemicals is $\sim$10.5 R, which is known as Trouton's Rule.

Next, we ascertain whether entropy is a state function, which as explained in sec. 2.2 means that the entropy content of a system is independent of how the system was prepared. As a result, if entropy is a state function, then a change of entropy is independent of how the change occurs (so called "path independence"). It would seem at first that this is unlikely, because heat itself is path dependent which is why the partial change in heat ∂q is an inexact differential as explained in sec. 2.4. It seems that $\frac{\partial q}{T}$ might likewise be inexact. Let's see if it is by applying Euler's test for exactness: `\left( \dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x=\left( \dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y`. Starting with:

$$\partial U=\partial q+\partial w$$

we will assume a reversible path is followed ($\partial w=-P\partial V$) because ∂U is exact and it is legit to use any path we want. We will also insert $C_V\partial T$ for ∂U. Some rearrangement yields:

$$\partial q=C_V\partial T\ +P\partial V$$

Dividing by T yields:

$$\frac{\partial q}{T}=\frac{C_V}{T}\partial T\ +\frac{P}{T}\partial V$$

When we juxtapose the above against the definition of a change of a function $\partial f=\left(\frac{\partial f}{\partial x}\right)_y\partial x+\left(\frac{\partial f}{\partial y}\right)_x\partial y$:

we see that f = $\frac{q}{T}$, x = T, y = V, `\left( \dfrac{\partial f}{\partial x} \right)_y={\frac\left( \dfrac{\partial q}{T}}{\partial T} \right)_V=\frac{C_V}{T}` and `\left( \dfrac{\partial f}{\partial y} \right)_x={\frac\left( \dfrac{\partial q}{T}}{\partial V} \right)_T=\frac{P}{T}`.

When the Euler test for exactness: `\left( \dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x=\left( \dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y` is applied to $\frac{\partial q}{T}$ using these definitions:

`\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial q}{T}}{\partial T} \right)_V)}_T=\left( \dfrac{\partial }{\partial T}{\frac{\frac{\partial q}{T}}{\partial V} \right)_T)}_V \nonumber`

The right-hand term can be evaluated as: `\left( \dfrac{\partial }{\partial T}{\frac{\frac{\partial q}{T}}{\partial V} \right)_T)}_V=\left( \dfrac{\partial }{\partial T}\frac{P}{T} \right)_V` since `{\frac\left( \dfrac{\partial q}{T}}{\partial V} \right)_T=\frac{P}{T}`, and using the perfect gas law we can show that: `{\frac\left( \dfrac{\partial P}{T}}{\partial T} \right)_V=\frac{\partial nR/V}{\partial T}=0` Pa/K^2.

The left-hand side: `\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial q}{T}}{\partial T} \right)_V)}_T` requires more examination. We are going to work this derivation in a slightly more complex fashion this time by ignoring the fact that `{\frac\left( \dfrac{\partial q}{T}}{\partial T} \right)_V=\frac{C_V}{T}`, and instead note that $\partial U=\partial q$ at constant volume because no work is done. Dividing by temperature means $\frac{\partial U}{T}=\frac{\partial q}{T}$, which makes the left side: `\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial q}{T}}{\partial T} \right)_V)}_T=\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial U}{T}}{\partial T} \right)_V)}_T`. Next we can switch the order of differentiation from $\frac{\partial}{\partial V}\frac{\partial}{\partial T}$ to $\frac{\partial}{\partial T}\frac{\partial}{\partial V}$ since U is exact:

`\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial U}{T}}{\partial T} \right)_V)}_T=\left( \dfrac{\partial }{\partial T}{\frac{\frac{\partial U}{T}}{\partial V} \right)_T)}_V \nonumber`

which is an application of the Euler Test. It turns out that \({\frac\left(\dfrac{\partial U}{T}}{\partial V} \right)_T=)0 J/K/m^3 because at constant temperature $\partial U=0\ J$ (and thus the numerator $\frac{\partial U}{T}$ is likewise 0 J/K). Consequently, we can rework the left-hand side of the Euler test as:

`\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial q}{T}}{\partial T} \right)_V)}_T={\frac{\partial }{\partial V}0)}_T=0\ J/K^2/m^3 \nonumber`

Note that the units of J/K^2/m^3 are the same as \(Pa/K^{2}\) from the right-hand side of the Euler test. Thus, $\frac{\partial q}{T}$ is exact because it passes the test, here:

`\left( \dfrac{\partial }{\partial V}{\frac{\frac{\partial q}{T}}{\partial T} \right)_V)}_T=0\frac{J}{K^2m^3}=0\frac{Pa}{K^2}=\left( \dfrac{\partial }{\partial T}{\frac{\frac{\partial q}{T}}{\partial V} \right)_T)}_V \nonu`

Now that we are done making our eyes bleed due to the calculus, if it is acceptable that $\frac{\partial q}{T}$ is exact then we can accept that $\partial S=\frac{\partial q}{T}$ and$partialq=T\partial S$. However, we had to use the reversible path when applying the Euler test to $\frac{\partial q}{T}$, and thus:

$$\partial S=\frac{\partial q_{rev}}{T}\tag{4.1.1}$$

This makes the change in entropy path independent, which must be the case if ∂S is exact.

The fact that $\partial q_{rev}=T\partial S$ reveals new thermodynamic relationships. For example, we can calculate the change ∂U for any reversible or irreversible process. However, as internal energy is a state function, changes in U can always be calculated using the reversible path even for irreversible transitions! Hence, $\partial U=\partial q_{rev}+\partial w_{rev}$, which means:

$$\partial U=T\partial S-P\partial V\tag{4.1.2}$$

Likewise:

$$\partial H = \partial U + \partial(PV) = T\partial S - P\partial V + P\partial V + V\partial P = T\partial S + V\partial P \tag{4.1.3}$$

which is the same as derived before (Equation ???) except here we incorporate Equation 4.1.2. This is also consistent with the fact that enthalpy is a state function, and as such ∂H can always be calculated using the reversible path. Equations 4.1.2 and 4.1.3 are very useful relationships that we will make much more use of in the future.

4.2: Entropy inside and outside- The 2nd Law and the Clausius Inequality

Entropy change is intimately related to heat exchange, which is defined as thermal energy transferred between the system and surroundings. For example, if a system gains $+\partial q$ of heat from the exterior, then the exterior must have lost $-\partial q$ of heat. Thus it must be true that both the system and surroundings have also gained / lost entropy, and the sum is the total change of entropy. In fact let's call this the total entropy change of the Universe. This is important because the 2^{nd} Law of Thermodynamics states:

The entropy of the Universe is always increasing.

Therefore, it is important to calculate the entropy changes in both the system and the surroundings that are exterior to the system. Before we discuss this further, it must be stated that the somewhat simplistic definition $\partial S = \frac{\partial q_{rev}}{T}$ does not fully describe all the ways that entropy can increase. To illustrate, let's say a system gains $\frac{\partial q_{rev}}{T}$ amount of entropy from the surroundings. Thus, the surroundings must have lost $\frac{-\partial q_{rev}}{T}$ worth of entropy. As a result, it appears that the total change in entropy for any heat exchange process is: $\Delta S_{tot} = \frac{\partial q_{rev}}{T} - \frac{\partial q_{rev}}{T} =$ 0 J/K. However, *this isn't necessarily true*; for example, imagine our system is a tin can full of water, and heat is added by the exterior from a candle placed underneath it as in Figure 2.1A. There is an increase the entropy of the system as calculated by $\frac{\partial q_{rev}}{T}$. But the setup is very inefficient as a lot of the heat from the candle is not delivered into the system, rather is just wanders off and remains in the exterior. This means that the change in the entropy of the outside is greater than $\frac{-\partial q_{rev}}{T}$ (meaning it is a less negative number) and thus the sum of the interior and exterior entropy is greater than 0 J/K. You may have figured out already that if we had a perfectly efficient way to input heat from the exterior to the interior, such as that shown in Figure 2.1B, then the total entropy change would in fact be 0 J/K. In the next section will discuss further the differences between inefficient and efficient heating, which is related to reversibility just like we encountered when discussing work in Sec. 2.2.

4.2.1 Reversible and irreversible heat exchange. Here we define how an efficient exchange of thermal energy is reversible, whereas a "lossy" (or inefficient) energy exchange is irreversible. To do so we review work from Section 2.2, where we demonstrated graphically how reversible work is always more negative than irreversible. Mathematically this means $\partial w_{irrev} > \partial w_{rev}$. To cast a wider net, for any type of work (∂w) we can state $\partial w \geq \partial w_{rev}$, as we don't specify whether ∂w is reversible or irreversible; the equivalence exists in the case of the process being reversible.

Next we consider an isothermal process, which means that $\partial U = \partial q + \partial w = 0\ J$ because of the Equipartition theorem. Thus the heat exchanged (∂q) is equal to the negative of work:$partialq = -\partial w$, and as a result anything true for work then the opposite is true of heat. Consequently, if $\partial w \geq \partial w_{rev}$, then:

$$\partial q_{rev} \geq \partial q$$

and note that we have not stated whether the heat exchange of the process is reversible or irreversible, and the equivalency is in the event we are describing a reversible heat exchange. If we divide both sides of the above by T: \(\frac

ParseError: invalid DekiScript (click for details)

{T}\ge \frac{\partial q}{T}\), we see that:

$$\partial S \geq \frac{\partial q}{T}$$

due to the definition of the change in system entropy as \(\partial S=\frac

ParseError: invalid DekiScript (click for details)

{T}\), Equation 4.1. If we subtract $\frac{\partial q}{T}$ from both sides:$\partial S - \frac{\partial q}{T} \geq 0\ J/K$

This is the famous Clausius Inequality, and of course the equality holds if the process is reversible.

Here is where we have to discuss interior and exterior changes of entropy further. For the system to experience a heat exchange ∂q with the exterior, it must be true that the exterior experienced a heat exchange of -∂q. As a result, it must also be true that the change in the exterior entropy is $\partial S_{exterior} = \frac{-\partial q}{T}$. Now let's revise the statement $\partial S - \frac{\partial q}{T} \geq 0\ J/K$ as:

$$\partial S + \partial S_{exterior} \geq 0\ J/K$$

given that $\partial S_{total} = \partial S + \partial S_{exterior}$:

$$\partial S_{total} \geq 0\ J/K \tag{4.2.1}$$

It seems that we have proven the 2^{nd} Law! In fact, we call something "spontaneous" for any process for which the total entropy increases; this is a fancy way of saying that "it happens". Spontaneous processes include buildings falling down and the cat tearing up the furniture. Likewise, a process that would result in total entropy decreasing could never occur. An example is cooling popcorn back into the form of a kernel. As such, we can understand that the 2^{nd} Law means $\partial S_{total} \geq 0\ J/K$, where the equality sign applies to systems at equilibrium.

To make more progress on our understanding of the 2^{nd} Law, let's go back to Equation 4.4: $\partial S - \frac{\partial q}{T} \geq 0\ J/K$ and multiply both sides by –T:

$$\partial q - T\partial S \leq 0\ J$$

(the greater than / equal sign has been reversed, which occurs because –T is always negative.) While we wish we could make more of the relationship above, we can't unless we have more information on the thermodynamic process being investigated. For example, we can stipulate that the process is occurring at constant volume. Since the change in internal energy is: $\partial U = \partial q + \partial w$, and no work can be done at constant volume, then $\partial U = \partial q$. Now we are left with:

$$\partial U - T\partial S \leq 0\ J$$

and… so what? The above still doesn't mean too much unless we make another stipulation concerning the nature of the process. This time we choose to state that there is no change in the system entropy ($\partial S = 0\ J/K$). Now:

$$\partial U \leq 0\ J$$

At this point we can make a "big picture" statement. Recall that the derivation of the above began with: $\partial S_{total} \geq 0\ J/K$, which again means that the total entropy of a spontaneous process increases. At the end of the derivation we demonstrated that internal energy must decrease or stay the same ($\partial U \leq 0\ J$). But what does that mean? For example, what happens if internal energy rises? Since we started this derivation with the statement about how a spontaneous process has an increase in total entropy, we ended the derivation *still discussing what makes a process spontaneous*. Which is, for a system under constant volume and constant system entropy, the internal energy must decrease for a process to be spontaneous.

Let's go back to the step in the derivation before we stipulated a constant volume process was at play: $\partial q - T\partial S \leq 0\ J$. What if we were examining a constant pressure system instead? In that case, as we showed in Sec. 3.1: $\partial H = \partial q$. Now we have:

$$\partial H - T\partial S \leq 0\ J$$

and if we stipulate that the process occurs at a constant system entropy:

$$\partial H \leq 0\ J$$

Now we see that, for a process to be spontaneous under conditions of constant pressure and constant system entropy, the enthalpy must decrease.

To recap, we have accepted the fact that $\partial S_{total} \geq 0\ J/K$ for a process to be spontaneous, which is equivalent to $\partial U \leq 0\ J$ under conditions of constant volume and system entropy. However, if the process occurs under constant pressure and system entropy then it must be true that $\partial H \leq 0\ J$. Now do you recall learning in Freshman Chemistry that Gibb's energy must be negative (i.e. $\partial G \leq 0\ J$) for a process to be spontaneous? Did we just up-end that? We did, and we will explain this discrepancy in the next chapter. Until then there is another facet of entropy that we have to explore concerning the efficiency of car engines and why planes fly at 35 thousand feet.

4.3: Calculating Entropy Changes

While the partial change of entropy is \(\partial S=\frac

ParseError: invalid DekiScript (click for details)

{T}\), we must integrate it to measure a finite, quantifiable result:

\[\Delta S=\int{}\partial S=\int{}\frac

ParseError: invalid DekiScript (click for details)

{T} \nonumber \]

This seems overly easy, especially as we know that nothing is so simple due to the existence of four classes of thermodynamic changes (reversible or irreversible $\times$ adiabatic or isothermal). We might expect a different way of calculating ΔS for each one; however, this isn't the case since S is a state function as described in the following sections.

4.3.1 Changes in System Entropy

Let's start with isothermal, reversible transitions. Isothermal makes T constant, which means that the integral expression above can be simplified by taking the temperature outside of the integral:

\[\Delta S_{isoT,rev}=\int{}\frac

ParseError: invalid DekiScript (click for details)

{T}=\frac{1}{T}\int{}{\partial q}_{rev}=\frac{1}{T}\cdot {\Delta q}_{rev} \nonumber \]

Recall that, under isothermal conditions $\Delta U=0\ J$, which when coupled with reversibility means $\Delta U=\Delta q_{rev}+\Delta w_{rev}=0\ J$, and thus $\Delta q_{rev}=-\Delta w_{rev}=nRT\cdot\ln\left(\frac{V_f}{V_i}\right)$ according to our learnings in Section 2.2. As a result: $\Delta S_{isoT,rev}=\frac{1}{T}\cdot nRT\cdot\ln\left(\frac{V_f}{V_i}\right)=nR\cdot\ln\left(\frac{V_f}{V_i}\right)$

As for isothermal and irreversible, since ΔS is path-independent the result is the same: $\Delta S_{isoT,irrev}=nR\cdot\ln\left(\frac{V_f}{V_i}\right)$. Path independence sure makes our lives easier!

We now move onto to adiabatic transitions. These calculations should be easy because $\partial q_{ad}=0\ J$ regardless whether we are doing a reversible or an irreversible transition. And while it appears that there should be no change in the system entropy, in fact this isn't quite true. Recall that we previously stated that the definition of the change in entropy from Equation 4.1: \(\partial S=\frac

ParseError: invalid DekiScript (click for details)

{T}\) is deficient. To analyze what this really means, let's use the fact that changes in entropy are exact and we can examine adiabatic transitions using two separate steps as shown in Figure 4.2. Under adiabatic conditions both the volume and temperature of the system are affected. As shown in Fig. 4.2 first there is an isothermal change in volume (Path 1), for which we have already determined: $\Delta S_1=nR\cdot\ln\left(\frac{V_f}{V_i}\right)$. In the second step there is a change in temperature under conditions of constant volume. This can only be accomplished through a heat exchange, for which the relevant relationship is: $\partial q=C_V\partial T$ which is true whether the transition is reversible or not. Thus:

\[{\Delta S}_2=\int{}\frac

ParseError: invalid DekiScript (click for details)

{T}=\int{}\frac{C_V\partial T\ }{T} \nonumber \]

The above needs to be converted into a definite integral, the limits of which have the units of the partial (temperature). If we assumed the heat capacity is independent of temperature:

$$\Delta S_2 = C_V \cdot \int_{T_i}^{T_f} \frac{1}{T} \cdot \partial T = C_V \cdot \ln\left(\frac{T_f}{T_i}\right)$$

Since $\Delta S = \Delta S_1 + \Delta S_2$ as shown in Figure 4.2, the final result is:

$$\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) \tag{4.3.1}$$

Here is some good news- due to the fact that entropy is exact, the equation 4.6 is always “the answer”. It works for every transition; for example, in an isothermal transition the 2^{nd} term is missing ($\ln(1) = 0$), leaving us what we derived in the beginning of this section: $\Delta S_{isoT} = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$.

There are some nuances for calculating ΔS via Equation 4.6 for adiabatic systems. For example, we already stated that it may appear $\Delta S_{ad} = 0\ J/K$ for all adiabatic transitions because $\partial q_{ad} = 0\ J$ always. To explore further we will calculate the adiabatic reversible $\Delta S_{ad,rev}$ using the adiabatic equation of state: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ from Equation 2.13, section 2.5.1.1. A small rearrangement yields: $\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}}$, which we can insert into Equation 4.6 for ΔS:

$$\Delta S_{ad,rev} = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left[\left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}}\right]$$

Using the identities $\ln(a^b) = b \cdot \ln(a)$ and $\ln\left(\frac{a}{b}\right) = -\ln\left(\frac{b}{a}\right)$ gives us:

$$\Delta S_{ad,\ rev} = -nR \cdot \ln\left(\frac{V_i}{V_f}\right) + C_V \cdot \frac{nR}{C_V} \cdot \ln\left(\frac{V_i}{V_f}\right) =$$

$$-nR \cdot \ln\left(\frac{V_i}{V_f}\right) + nR \cdot \ln\left(\frac{V_i}{V_f}\right) = 0\ J/K$$

Thus, the system entropy change for adiabatic reversible transitions is $0\ J/K$. In fact, if you are asked to analyze an adiabatic reversible transition and you correctly apply all the final and initial variables into Equation 4.6 using your calculator, you will find $\Delta S = 0\ J/K$ although as always be careful with significant figures!

The adiabatic irreversible situation is not so simple. Since the adiabatic reversible equation of state does not apply in the irreversible situation, then it is impossible for the changes in volume and temperature to balance out perfectly. In other words:

$$\Delta S_{ad.,irrev.} = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) \neq 0\ J/K$$

To solve entropy changes for adiabatic irreversible transitions, one has to calculate the change in volume and temperature using $C_V \Delta T = -P_{ext} \Delta V$ as shown in Section 2.5.1.2, and then insert the results into Equation 4.6. If calculated correctly, you will always find that $\Delta S_{ad,irrev} > O\ J/K$. As a result, this reveals a small flaw with the expression \(\partial S=\frac

ParseError: invalid DekiScript (click for details)

{T}\), which implies that there no changes to system entropy under adiabatic but this is not true. Chemical Engineers have long recognized this issue and resolved it by defining changes in entropy as: \(\partial S=\frac

ParseError: invalid DekiScript (click for details)

{T}+{\partial S}_{added}\). The 2^{nd} term is designed to account for the adiabatic irreversible condition, although unfortunately it doesn't help you actually perform any calculations!

4.3.2 Changes in Exterior Entropy

In the previous section we discussed how $\partial S_{total} \geq 0\ J/K$ according to the 2^{nd} Law, where the equality is for systems at equilibrium. Here we use this expression to determine how the exterior entropy changes as a function of conditions (isothermal or adiabatic × reversible or irreversible). We will start with the adiabatic case, which is the easiest to calculate. As adiabatic means there is no heat exchange with the exterior, then it must be true that $\partial S_{ext} = 0\ J/K$ regardless of whether the transition is reversible or irreversible. Consequently, adiabatic reversible have a total entropy change of $\partial S_{total} = \partial S_{ext} + \partial S = 0\ J/K$. Likewise, the total change in entropy in the adiabatic irreversible case is $\partial S_{total} = \partial S > 0\ J/K$, since the total is equal to the system's change in entropy given the lack of an exterior interaction.

Concerning isothermal transitions, we will start with the reversible which experiences a heat exchange ∂q_{rev} with the exterior. The resultant change in system entropy is \(\partial S=\frac

ParseError: invalid DekiScript (click for details)

{T}\). Likewise, the exterior experiences a $-\partial q_{rev}$ with the system and has a change of entropy of \({\partial S}_{ext}=-\frac

ParseError: invalid DekiScript (click for details)

{T}\). Clearly, $\partial S_{tot} = \partial S + \partial S_{ext.} = 0\ J/K$, just like the adiabatic reversible. In fact, the definition of reversibility is $\partial S_{total} = 0\ J/K$! To be more specific, recall that we established the formula for isothermal change in system entropy, $\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$, which means that the exterior change is: $\Delta S_{ext} = -\Delta S = -nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. As for isothermal irreversible:

$$\partial S_{total} = \partial S_{ext} + \partial S > 0\ J/K$$

because $\partial S_{total} > 0\ J/K$ is the definition of an irreversible transition. Consequently, some middle-school algebra allows us to determine that: $\partial S_{ext} > -\partial S$. Integration of this relationship yields: $\Delta S_{ext} > -nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. This is actually where we stop because we do not have the ability to determine the exact change in ΔS_{ext}; we can only know that it is greater than the reversible system entropy change. This is because the exterior dynamics may due to some un-knowable action such that the total entropy increases to overcome any decrease in entropy of the system (or didn't decrease enough if the entropy of the system increases). For example, in irreversible heating with a candle as shown in Figure 2.1A, thermal energy is not fully transferred from the exterior (the candle) to the system (the cup of water). This is clearly inefficient and irreversible, and the "lost" energy must increase the exterior entropy more than could ever be discerned from the study of the system alone. Let's take another example, such as a system under compression due to the action of a piston. This lowers the system's entropy. But what actor on the outside of the system is responsible for compressing the piston? If a cat is doing it, then it is guaranteed that the exterior experienced a significant increase in entropy. And the magnitude of the total increase in entropy is unknowable, as any cat owner will tell you.

These results are summarized in Table 4.1. And with this information in our thermodynamics toolkit, we will now determine the theoretical efficiency of gas-burning motor vehicles.

Transition	ΔS (J/K)	ΔS_{ext} (J/K)	ΔS_{tot} (J/K)
Isothermal, reversible	$nR \cdot \ln\left(\frac{V_f}{V_i}\right)$	$-\Delta S$	0
Isothermal, irreversible	$nR \cdot \ln\left(\frac{V_f}{V_i}\right)$	$> -\Delta S$	> 0
Adiabatic, reversible	0	0	0
Adiabatic, irreversible	$nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right)$	0	ΔS

4.4: The Car Engine and the Carnot Cycle

When civilization began, people survived by the work of their hands. Farming meant pushing a plow, although the discovery of the mule made this easier. Later, the industrial revolution demonstrated the utility of machines for work. Unlike other people and mules, machines never tire and can be turned off and on at will, and their food is super-cheap. As this fuel is oil.

Machines burn fuel to do work, meaning $\partial q \rightarrow \partial w$, and this direction of energy flow has profound implications for engine efficiency. We must consider how to practically power a machine. When you were a baby your first interaction with a machine was likely a wind-up toy, perhaps a car. Compressing and releasing the toy's spring propelled the miniature vehicle forward, until the spring got sprung. Although this mechanism works just fine for a child's toy, would a company design a real car around the same principle? Such a vehicle wouldn't propel anyone very far before having to be wound up again, which would be clumsy at best (and the spring would have to be huge!). Overall, we reject the use of a spring-driven vehicle and prefer a car with a *reciprocating engine*.

A reciprocating engine uses heat to create work in a cyclical process (this is where the end state is the same as at the beginning). An example is a modern 4-stroke piston engine shown in Figure 4.3. A mixture of petroleum and air is drawn inside, compressed, and then ignited by a sparkplug. The resulting expansion pushes the piston downward in the power stroke, which turns the car's wheels that are connected by the crankshaft. Afterwards, the spinning crankshaft pushes the piston back into the original state, which expels the resultant CO_2 gas and water vapor out into the tailpipe in the process. More fuel and air are drawn in and burned as the cycle is repeated. The net work is negative, and also recall that expansion work is energy *out of the system*. Another, easier way to think of this is to ask yourself, would you rather be pushed forward or pulled (dragged) behind a car? Hopefully you said pushed forward, which means you want the reciprocating engine to produce a negative amount of work.

The idea of a reciprocating process was first realized in steam engines, which were becoming ubiquitous in 1830 when Sadi Carnot was in the French military. At that time Carnot was busy shooting cannon balls at things; this was his job in the military which made him wonder how heat is converted into work. Carnot imagined the simple system shown in Figure 4.4, whereby negative work is created by expanding a gas in cylinder body by placing it on a heat source. Afterwards, the system is returned to its initial volume by moving it onto a cold block. This simple model allowed Carnot to derive the theoretical efficiency of converting heat to work, which can be used to demonstrate that cars need both pistons and tailpipes and explains why planes fly at high altitudes. Carnot also introduced the concept of entropy (although he didn't use that word), and as a result Carnot is called the father of Thermodynamics. Carnot died soon after of cholera in 1832; I'm sure his cat was sad.

Carnot expanded on the simple model described above by developing an idealized cycle to represent a reciprocating engine shown in Figure 4.5. The piston initially has a small volume (V_1) and experiences an input of heat (Δq_1). The resulting high temperature and pressure ($T_{hot},\ P_1$) of gas expands the piston to create some negative, "pushing" type isothermal work (Δw_1). The system lands at volume V_2 and pressure P_2, still at T_{hot}. Note that the relevant thermodynamic quantities are defined in the figure. The next step is to lower the temperature, for which Carnot imagined using an adiabatic expansion to generate small bit more negative work (Δw_2) to take the system to volume V_3 and pressure P_3. The adiabatic expansion cools the cylinder to a lower temperature, T_{cold}. To compress the piston back to the original state, Carnot simply reversed the first two steps using an isothermal reversible compression that releases heat followed by an adiabatic compression to return it to $T_{hot},\ P_1$, and V_1.

4.4.1 Efficiency of the Carnot Cycle

The Carnot cycle is clever in how it forms a perfect loop. Here we perform a thermodynamic analysis to understand the implications of a cyclical hot expansion followed by a cold compression. First, we add up the total work performed by the cycle, which is:

$$\Delta w_{tot} = \Delta w_1 + \Delta w_2 + \Delta w_3 + \Delta w_4$$

where $\Delta w_1 = -nRT_{hot} \cdot \ln\left(\frac{V_2}{V_1}\right)$ $;Deltaw_2 = C_V \cdot (T_{cold} - T_{hot})$; $\Delta w_3 = -nRT_{cold} \cdot \ln\left(\frac{V_4}{V_3}\right)$; and $\Delta w_4 = C_V \cdot (T_{hot} - T_{cold})$. Obviously $\Delta w_2 = -\Delta w_4$, so these cancel out and the total work is now composed of just two terms:

$$\Delta w_{tot} = \Delta w_1 + \Delta w_3 = -nRT_{hot} \cdot \ln\left(\frac{V_2}{V_1}\right) - nRT_{cold} \cdot \ln\left(\frac{V_4}{V_3}\right)$$

This can be simplified if we can demonstrate a relationship between $\ln\left(\frac{V_2}{V_1}\right)$ and $\ln\left(\frac{V_4}{V_3}\right)$, which we will do using the adiabatic expansion and compression steps that connect state 2 to 3 and state 4 to the initial state 1, respectively. Specifically, the adiabatic equation of state $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ stipulates that, in the 2^{nd} step:

$$\left(\frac{T_{cold}}{T_{hot}}\right)^{\frac{C_V}{nR}} = \frac{V_2}{V_3}$$

and in the 4^{th} step: $\left(\frac{T_{hot}}{T_{cold}}\right)^{\frac{C_V}{nR}} = \frac{V_4}{V_1}$ which can be inverted into:

$$\left(\frac{T_{cold}}{T_{hot}}\right)^{\frac{C_V}{nR}} = \frac{V_1}{V_4}$$

which means: $\frac{V_2}{V_3} = \frac{V_1}{V_4}$ and can be rearranged to: $\frac{V_2}{V_1} = \frac{V_3}{V_4}$. Taking the natural log of both sides:

$$\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_3}{V_4}\right) = -\ln\left(\frac{V_4}{V_3}\right)$$

since $-\ln\left(\frac{a}{b}\right) = \ln\left(\frac{b}{a}\right)$. This allows us to substitute: $+nRT_{cold}\cdot\ln\left(\frac{V_2}{V_1}\right)$ for: $-nRT_{cold}\cdot\ln\left(\frac{V_4}{V_3}\right)$ in the equation for total work:

$$\Delta w_{tot} = -nRT_{hot}\cdot\ln\left(\frac{V_2}{V_1}\right) - nRT_{cold}\cdot\ln\left(\frac{V_4}{V_3}\right)$$

$$= -nRT_{hot}\cdot\ln\left(\frac{V_2}{V_1}\right) + nRT_{cold}\cdot\ln\left(\frac{V_2}{V_1}\right) = -nR\cdot\ln\left(\frac{V_2}{V_1}\right)(T_{hot} - T_{cold})$$

Since $V_2 > V_1$ and $T_{hot} > T_{cold}$, clearly Δw_{tot} is a negative quantity. Perhaps this seemed to be a large amount of effort to demonstrate a point than can be proven graphically as shown in Figure 4.6 (left), which is an exaggeration of the Carnot cycle. Here, the graph of P vs. V clearly has more area under the hot expansion compared to the cold compression, which is consistent with the generation of net negative work.

Next we determine the efficiency of the Carnot cycle, although we must make some decisions on what “efficiency” means. Since modern engines turn heat into work, it seems that we should determine the ratio of the total work divided by the heat: $\frac{\Delta w_{tot}}{\Delta q_{tot}}$, where the total heat is the sum of the 1^{st} and 3^{rd} steps. However, this isn’t quite right. To understand, note that in the 1^{st} expansion step we add the heat energy which takes action on our part plus fuel (which means \[s!). In contrast, the 3^{rd} compression step loses heat which doesn’t take any effort from us, the engine user. In an actual motor vehicle the 3^{rd} step is when the exhaust gas in the engine is opened to the tailpipe, which dissipates the leftover heat all on its own. Thus, efficiency should be the total work divided by just the heat added in the 1^{st} step (Δq_1). As that the total work is also negative, so we are going to define the efficiency as the absolute value of the work to heat ratio:

$$Efficiency = \left|\frac{\Delta w_{tot}}{\Delta q_1}\right| \tag{4.4.1}$$

Using the equations derived previously the efficiency is:

$$\left|\frac{\Delta w_{tot}}{\Delta q_1}\right| = \left|\frac{-nR\cdot\ln\left(\frac{V_2}{V_1}\right)(T_{hot} - T_{cold})}{nR\cdot\ln\left(\frac{V_2}{V_1}\right)(T_{hot})}\right| = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$$

(If you are following along but have lost track of a minus sign in the numerator, that is the effect of the absolute value). A very important result of this relationship is that the Carnot cycle cannot be 100% efficient unless $\frac{T_{cold}}{T_{hot}} \sim 0$. This is a bit of a bummer, and it also shows us that those wacky Youtube videos of perpetually motion contraptions are impossible. So how can we make a machine at least more efficient, to save money and use less fuel? We try to make the ratio $\frac{T_{cold}}{T_{hot}}$ as low as possible. For example, we can increase the temperature in the engines, unless it gets so hot that it melts. As for the cold sink, do you see now why airplanes what fly at ~30 K feet where the atmospheric temperature is quite low (-55 $^\circ$C)? Overall, one of the values of such thermodynamic analyses as presented here is that our fundamental understandings of science and nature help us manipulate our surroundings to be of maximum benefit to us and the environment.

Equation 4.4.1 reveals more about the inner workings of reciprocating engines by the fact that the efficiency is 100% if the cold block (i.e. car tailpipe) is at 0 K. How can a cold tailpipe affect mechanical motion such that all the heat energy is converted into work? Recall that all the work is performed by a gas. Using the perfect gas law: $PV = nRT_{cold}$ with $T_{cold} = 0\ K$ in cycle steps 3 and 4 means that the exterior pressure in those compressions is 0 Pa. In other words, the system is compressing against a vacuum to return to the original state, and since $\partial w = -P_{ext}\partial V$, this isn't any work at all! This situation is depicted in Figure 4.6, which makes it clear that the lack of perfect efficiency of the Carnot cycle is due to the loss of energy when performing compression work to return the system back to the original state.

A relevant practice problem is provided in Example Problem 4.1. Here you can see that the input of energy into an adiabatic reversible device results in negative work out of the system. Consistency with the second law is demonstrated by the fact that there is no change in total entropy (in or out the system!). This makes the work out the most possible, which is nonetheless less than the input energy of heat. Hence, machine efficiency is finite. Upon closer analysis the efficiency of the transition $\left(\left|\frac{\Delta w_{tot}}{\Delta q_1}\right| = \frac{32.1\ J}{100\ J}\right)$ appears greater than allowed from our analysis of the Carnot cycle: $\left(1 - \frac{T_{cold}}{T_{hot}}\right)$; however, the example problem doesn't follow a full Carnot cycle because we didn't make the piston transform back into its original state. If we had, work would have been lost in the compression.

4.4.2 Entropy of the Carnot Cycle

While we have demonstrated that a Carnot cycle cannot be 100% efficient, at least not practically, we now ask the question: so what? Just like I'm not concerned about the efficiency of a wind-up spring toy, perhaps the Carnot cycle describes a mechanical system that is not of interest. To show why this isn't the case, we must calculate the total change in system entropy of the Carnot cycle by summing up the changes. As steps 2 & 4 are adiabatic and reversible, there is no change in entropy at all (see Table 4.1 on pg.); thus $\Delta S_{2+4} = 0\ J/K$. As for steps 1 & 3, as these are isothermal reversible transitions:

$$\Delta S_1 + \Delta S_3 = nR \cdot \ln\left(\frac{V_2}{V_1}\right) + nR \cdot \ln\left(\frac{V_4}{V_3}\right)$$

While we can't make much headway with this, note that we previously determined that $\ln\left(\frac{V_2}{V_1}\right) = -\ln\left(\frac{V_4}{V_3}\right)$ using the adiabatic equation of state. Thus:

$$\Delta S_1 + \Delta S_3 = -nR \cdot \ln\left(\frac{V_4}{V_3}\right) + nR \cdot \ln\left(\frac{V_4}{V_3}\right) = 0\ J/K$$

Consequently, the entropy change of the system throughout the cycle is $\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 0\ J/K$. Now we can consider the exterior changes in entropy. First, $\Delta S_{ext,2} + \Delta S_{ext,4} = 0\ J/K$ since these steps are adiabatic, and likewise $\Delta S_{ext,1} + \Delta S_{ext,3} = 0\ J/K$ because of the reversibility of those steps. As a result, the total $\Delta S_{ext} = 0\ J/K$ and thus $\Delta S_{tot} = 0\ J/K$. This means that the Carnot cycle is fully reversible. As reversible systems provide the most exterior (negative) work as we established in Sec. 2.2, it must be true that an engine that operates by the Carnot cycle is the most efficient engine that could ever exist. As a result, we can now stipulate that, for any machine a person could ever build, that efficiency is less than $\left(1 - \frac{T_{cold}}{T_{hot}}\right)$; this is the most important result of thermodynamics.

4.5: Refrigeration

The flow of heat from a hot source to a cold sink is spontaneous, which you now know means that the total entropy increases. To demonstrate, let’s imagine that a hot metal block is placed next to a cold one. Initially the hot block loses $-\partial q$ of thermal energy of which $+\partial q$ is gained by the cold one. If we assume this occurs over a short period of time and the magnitude of the initial heat transaction is small, then the relative temperatures are assumed to remain constant. The absolute values of the entropy changes for each system have the following relationship:

$$\left|\frac{+\partial q}{T_{cold}}\right| > \left|\frac{-\partial q}{T_{hot}}\right|$$

due to the fact that $T_{hot} > T_{cold}$. As a result:

$$\Delta S_{total} = \Delta S_{cold} + \Delta S_{hot} = \frac{\partial q}{T_{cold}} - \frac{\partial q}{T_{hot}} > 0\ J/K$$

and the process is spontaneous; this is summarized in Figure 4.7.

Next we move on to your refrigerator, which is a freak of nature because heat flows the wrong way. As shown in Figure 4.7, energy must flow out of the cold reservoir (the refrigerator interior) to the hot exterior. Thus, the ∂q’s from our derivation above switch signs and the process is non-spontaneous: $\Delta S_{total} = \Delta S_{cold} + \Delta S_{hot} = \frac{\partial q}{T_{hot}} - \frac{\partial q}{T_{cold}} < 0\ J/K$. Since it is impossible for any process to decreases total entropy, we just proved refrigerators don’t exist.

Since you obey the laws of thermodynamics in your household, there is in fact a mechanism by which your refrigerator can transfer heat from cold to hot yet still generate a net positive change in total entropy. Shown in Figure 4.8 is a diagram of a refrigerator, where a cool gas flows in a continuous loop. The compressor liquefies the coolant, generating heat which is expelled out into the exterior. The liquid then flows past an expansion valve that causes the liquid to become gas, which is a phase change requiring an input of heat from interior of the system. For the remaining discussion, we assume that the closed loop is the system that experiences a positive input of heat ∂q_{cold} at T_{cold} and expels a negative quantity of heat ∂q_{hot} at T_{hot}.

To see how the system generates a net positive (or 0 J/K at a minimum) of total entropy, we first note that there is an input of work (the gas compression) that is turned into heat, the energy of which is fed into the flow from cold to hot as shown in Figure 4.8. As a result, the warmer exterior experiences a greater (+)heat exchange compared to the losses of (-)heat energy by the refrigerator interior. This means $|\partial q_{cold}| < \partial q_{hot}$ (recall that ∂q_{cold} is negative and ∂q_{hot} is positive, so we have to make comparisons to the absolute value of $|\partial q_{cold}|$), and thus the total entropy change is:

$$\Delta S_{total} = \Delta S_{cold} + \Delta S_{hot} = \frac{\partial q_{cold}}{T_{cold}} + \frac{\partial q_{hot}}{T_{hot}} \geq 0\ J/K$$

To summarize, refrigerators work because the heat flow to the exterior is increased to offset the effect of dividing by a larger value of temperature when calculating the entropy change.

4.5.1 Coefficient of performance

In a refrigerator the compressor is responsible for the input of work, which contributes to the relative efficiency of the system as defined by the coefficient of performance (COP):

$$COP = \frac{-\Delta q_{cold}}{\Delta w}$$

The COP defined as a positive quantity (hence -Δq_{cold} in the numerator, and Δw is positive), and is not quite the same thing as efficiency because it can be $>$100%. Of course a COP is desirable, and typical values are $\sim$2$\rightarrow$3. To derive the COP from these metrics of a refrigerator, we first note that conservation of energy requires:

$$\Delta w = \Delta q_{hot} - \Delta q_{cold}$$

as is obvious from Figure 4.8, and as a result $COP = \frac{-\Delta q_{cold}}{\Delta q_{hot} - \Delta q_{cold}}$. To understand the COP better, we need to demonstrate a relationship between the two heat transactions (Δq_{hot} andΔq_{cold}) with the refrigerator “cold” and exterior “hot” temperatures. To do so we will assume that the closed loop of coolant is as efficient as a Carnot engine, and that the 1st Carnot step is the input of heat into the cooling coil inside the refrigerator and the 3rd leg of the Carnot cycle represents the expulsion of heat into the exterior. From Figure 4.5 we see:

$$\frac{\Delta q_{cold}}{\Delta q_{hot}} = \frac{-\Delta w_1}{-\Delta w_3} = \frac{nRT_{cold} \cdot \ln\left(\frac{V_2}{V_1}\right)}{nRT_{hot} \cdot \ln\left(\frac{V_4}{V_3}\right)}$$

Since we showed in the previous section that: $\ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_3}{V_4}\right)$ then: $\frac{\Delta q_{cold}}{\Delta q_{hot}} = -\frac{T_{cold}}{T_{hot}}$, or:

$$\Delta q_{cold} = -\frac{T_{cold}}{T_{hot}} \Delta q_{hot}$$

Plugging the above into the equation for the COP yields:

`COP=\frac{\frac{T_{cold}}{T_{hot}}\Delta q_{hot}}{\Delta q_{hot}+\frac{T_{cold}}{T_{hot}}\Delta q_{hot}}=\frac{\frac{T_{cold}}{T_{hot}}}{1+\frac{T_{cold}}{T_{hot}}}=\frac{T_{cold}}{T_{hot}-T_{cold}}`

We can see that a higher COP can be achieved by minimizing the exterior and interior temperature differences. Too bad, as trying to cool a refrigerator more inherently makes it less efficient.

4.5.2 Thermoelectric Cooling

You may have heard of thermoelectric cooling devices, which are based on the Peltier effect that converts current directly into a temperature gradient. This effect occurs when two different materials are conjoined and current is forced through it, causing one side of the device to warm and the other to cool. While these solid-state devices may seem desirable for cooling as they have no moving parts, are small and lightweight, unfortunately, they are $\sim$1/4th as efficient (or worse) compared to conventional refrigerators. This is because the efficiency of the thermoelectric effect necessitates the use of materials that are highly electrically conductive yet minimally thermally conductive, which are two properties that are usually correlated. Researching new materials with a high thermoelectric efficiency is a current topic of research.

4.6: Maxwell Relationships

Before we go further in our analysis of entropy, the fact that reversible heating is $\partial q = T\partial S$ offers several opportunities for analysis that have been ignored thus far. For example:

$$\partial U = \partial q + \partial w = T\partial S - P\partial V$$

can be cast into the form of an exact differential:

$$\partial f\left(x,y\right) = \left(\frac{\partial f}{\partial x}\right)_y \partial x + \left(\frac{\partial f}{\partial y}\right)_x \partial y$$

which is exact because `\left( \dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x=\left( \dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y`

If we “line up” ∂U with ∂f:

then we can see that f=U, x=S, and y=V. This allows us to determine:

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial U}{\partial S}\right)_V = T$$

and:

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Now we can use the exactness of ∂U via the Euler Test:

`\left( \dfrac{\partial }{\partial V}{\frac{\partial U}{\partial S} \right)_V)}_S=\left( \dfrac{\partial }{\partial S}{\frac{\partial U}{\partial V} \right)_S)}_V \nonumber`

We insert $\left(\frac{\partial U}{\partial S}\right)_V = T$ on the left and $\left(\frac{\partial U}{\partial V}\right)_S = -P$ on the right to reveal:

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{-\partial P}{\partial S})_V \tag{4.6.1}$$

Equation 4.6.1 is a Maxwell relation, which can be used to derive thermodynamic proofs that would otherwise be difficult or impossible to evaluate by any other means.

Since we determined the above using ∂U, then what about$partial H$? Is there another Maxwell relationship? Starting with $\partial H = T\partial S + V\partial P$, which is an exact differential, and thus we follow similar steps as before to find: `\left( \dfrac{\partial }{\partial P}{\frac{\partial H}{\partial S} \right)_P)}_S=\left( \dfrac{\partial }{\partial S}{\frac{\partial H}{\partial P} \right)_S)}_P` which leads to:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4.6.2}$$

In the next chapter we will derive two more. In the meantime, let’s see what these Maxwell relations are good for!

4.6.1 Using Maxwell Relations

Equations 4.6.1 and 4.6.2 related changes in state variables under conditions of constant system entropy S due to the $\left(\frac{\partial T}{\partial V}\right)_S$ and $\left(\frac{\partial T}{\partial P}\right)_S$ terms. This means that they can only be applied for systems for which $\Delta S = 0\ J/K$, which is only true of adiabatic reversible transitions. Furthermore, it is always true that $\Delta S_{ext} = 0\ J/K$ for adiabatic systems due to the lack of heat exchange, which makes $\Delta S_{tot} = 0\ J/K$. Since there is no change in total entropy, the Maxwell relations in eqs. 4.9 and 4.10 represent equilibrium.

The utility of eqs. 4.9 and 4.10 is that it will allow us to calculate changes in the state variables volume, temperature, and pressure. Normally such derivatives $\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial P}{\partial T}\right)_V$, and $\left(\frac{\partial P}{\partial V}\right)_T$ are trivial to calculate using the perfect gas law; however, they do not apply to adiabatic (equilibrium) systems since P, V, and T are all simultaneously changing. As such, the purpose of this section is to determine $\left(\frac{\partial V}{\partial T}\right)_S$, $\left(\frac{\partial P}{\partial T}\right)_S$, and $\left(\frac{\partial P}{\partial V}\right)_S$ for systems at equilibrium.

4.6.1.1 Maxwell relation approach:

$\left(\frac{\partial V}{\partial T}\right)_S$. First let us tackle changing volume with temperature, although we must note that there are multiple ways to perform such a derivation. We will use Equation 4.9: $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\partial P}{\partial S})_V$, and in the next section we will demonstrate the same derivation using a slightly easier approach. The first step here is to invert Equation 4.9 as:

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{\partial S}{\partial P})_V$$

so now we are trying to solve $-\frac{\partial S}{\partial P})_V$. As $\partial U = T\partial S - P\partial V$, we solve for the change in entropy:

$$-\partial S = -\frac{1}{T}\partial U + \frac{P}{T}\partial V$$

This expression can be divided by ∂P, after which we apply the condition of constant volume:

$$-\frac{\partial S}{\partial P})_V = -\frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V + \frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_V = -\frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V$$

because $\frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_V = 0\ m^3/K$ due to the condition of constant volume ($\partial V = 0\ m^3$). Substituting $\partial U = C_V \partial T$, we find:

$$-\frac{\partial S}{\partial P})_V = -\frac{1}{T}\left(\frac{\partial U}{\partial P}\right)_V = -\frac{C_V}{T}\left(\frac{\partial T}{\partial P}\right)_V = -\frac{C_V}{T}\frac{V}{nR} = -\frac{C_V}{P}$$

where we used $\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{nR}$ and $\frac{V}{nRT} = \frac{1}{P}$ from the perfect gas law. As: $\left(\frac{\partial V}{\partial T}\right)_S = -\frac{\partial S}{\partial P})_V$ and $-\frac{\partial S}{\partial P})_V = -\frac{C_V}{P}$, we can now show that:

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{P} \tag{4.6.3}$$

Clearly the derivative is negative. This means that if one compresses the volume of an adiabatic system (∂V is negative), then the temperature rises (∂T is positive). Of course we already knew this about thermally insulated systems!

4.6.1.2 Alternative approach:

$\left(\frac{\partial V}{\partial T}\right)_S$. Given that we are examining changes in volume at constant system entropy entices me to study a different starting point: $\partial U = T\partial S - P\partial V$. Under adiabatic reversible conditions $\partial U = C_V\partial T$ and $\partial S = 0\ J/K$, leaving us with $C_V\partial T = -P\partial V$. A simple rearrangement yields $\frac{\partial T}{\partial V} = -\frac{P}{C_V}$, to which we must remember that we have already used the condition of constant entropy. Thus: $\left(\frac{\partial T}{\partial V}\right)_S = -\frac{P}{C_V}$, which rearranges to: $\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{P}$ as before.

4.6.1.3 Maxwell relation approach:

$\left(\frac{\partial P}{\partial T}\right)_S$. Similar to the previous example; starting with Equation 4.10: $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$, which as before is flipped over:

$$\left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$$

Thus, we need to determine $\left(\frac{\partial S}{\partial V}\right)_P$; to do so we use $\partial H = T\partial S + V\partial P$ to solve for entropy:

$$\partial S = \frac{1}{T}\partial H - \frac{V}{T}\partial P$$

Next, we divide by the change in volume: $\frac{\partial S}{\partial V} = \frac{1}{T}\frac{\partial H}{\partial V} - \frac{V}{T}\frac{\partial P}{\partial V}$ and now we apply constant pressure conditions:

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_P + \frac{V}{T}\left(\frac{\partial P}{\partial V}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial V}\right)_P$$

Where the 2^{nd} term is removed because $\frac{V}{T}\left(\frac{\partial P}{\partial V}\right)_P = 0\ Pa/K$ due to the condition of constant pressure ($\partial P = 0\ Pa$). Substituting $\partial H = C_P\partial T$:

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{T}\frac{P}{nR} = \frac{P\cdot C_P}{nRT} = \frac{C_P}{V}$$

where $\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{nR}$ and $\frac{P}{nRT} = \frac{1}{V}$ are from the perfect gas law. As: $\left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$ and $\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{V}$, we can now show that:

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V} \tag{4.6.4}$$

This derivative is always positive, which means that pressurizing a thermally insulated system increases the temperature.

4.6.1.4 Alternative approach:

$\left(\frac{\partial P}{\partial T}\right)_S$. Let's tackle $\left(\frac{\partial P}{\partial T}\right)_S$ again starting with the change in enthalpy: $\partial H = T\partial S + V\partial P$. Under adiabatic reversible conditions $partialS = 0\ J/K$ and $\partial H = C_P\partial T$, leaving us with $C_P\partial T = V\partial P$. A simple rearrangement yields: $\left(\frac{\partial T}{\partial P}\right)_S = \frac{V}{C_P}$. This of course rearranges to: $\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V}$ as we determined above.

4.6.1.5

$\left(\frac{\partial P}{\partial V}\right)_S$. This is a harder one because we don't have a good starting point. In this case, we use the Euler Chain formula: $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y$ as:

$$\left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial P}{\partial S}\right)_V$$

Here we incorporate eqs. 4.11 and 4.12: $\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S = \frac{P}{C_V}$ and $\left(\frac{\partial S}{\partial V}\right)_P = \frac{\partial P}{\partial T}\Big)_S = \frac{C_P}{V}$. Putting these together yields:

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{C_P}{C_V}\frac{P}{V} \tag{4.6.5}$$

Since the right side is composed of all positive quantities with a negative sign, then we see that pressure increases if volume decreases (and vice versa). While we already knew this, just like the examples above, it is nonetheless comforting to see that our derivations are consistent with the incredibly obvious. You can also use such derivations to determine how adiabatic systems respond to pressure and temperature changes. For example, if we rearrange Equation 4.13 as $\frac{\partial P}{P} = -\frac{C_P}{C_V}\frac{\partial V}{V}$ and integrate we discover:

$$\ln\left(\frac{P_f}{P_i}\right) = -\frac{C_P}{C_V}\ln\left(\frac{V_f}{V_i}\right)$$

which can be manipulated further into the form: $\frac{P_f}{P_i} = \left(\frac{V_i}{V_f}\right)^{\frac{C_P}{C_V}}$

Note that you can also arrive at this result using the adiabatic equation of state: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$ from section 2.5.1.1 by substituting in the perfect gas law for the temperatures; in fact the example problem on pg. demonstrates this exact derivation.

Conclusion. Entropy is unequivocally the most important thermodynamic variable. And now you see that energy is not as important as you thought; in fact, all it does is allow you to measure total entropy changes more easily. Up until now all our thermodynamic understandings have come from internal energy and enthalpy, which have entropy as a natural variable. From here on, we will now study constant temperature processes using energy equations that have temperature as a natural variable. And in the process, we will use a Legendre transform to define a thermodynamic variable that you learned so much about in high school and Freshman chemistry- the Gibbs energy.

CHAPTER OVERVIEW

5: Helmholtz and Gibbs Energy

Entropy ultimately explains why things occur. By “occur”, we mean that a process is spontaneous and has a $\Delta S_{tot} > 0\ J/K$, where the total is the sum of system’s and surrounding’s entropy changes. Recall from the previous chapter that we can associate a negative change in energy with an increase in total entropy, so long as the natural variables of energy are held constant. Thus, spontaneous means $\Delta U < 0\ J$ if system entropy *and volume* do not change. However, *if instead pressure* and system entropy are held constant then a spontaneous process has a negative ΔH. In both cases we see that there cannot be a change in system entropy, which is only true for the adiabatic and reversible condition that describes systems at equilibrium. But what about all the other types of transitions? After all most things aren’t at equilibrium!

Before we consider what makes a non-equilibrium process spontaneous, first consider the following question: is the world adiabatic or isothermal? While you may be thinking about how the outside temperature changes during the seasons (hence the Earth is adiabatic), it is also true that our planet is not encapsulated in insulated glass wool like the flask in Figure 2.1. For the most part, we live in an isothermal system. Next: is the world at constant volume or constant pressure? As Earth is not enclosed in a metal box, we live in a constant pressure environment. Clearly we need to know what type of energy dictates whether a process is spontaneous under isothermal, constant pressure conditions, because internal energy and enthalpy aren’t it!

5.1: Helmholtz Energy (and The Clausius Inequality Pt. II)

Neither internal energy nor enthalpy are relevant under isothermal conditions, and we need to derive new functions of energy that have temperature as a natural variable. Previously we used Legendre transforms to accomplish this task- let's do so again!

Recall that volume and entropy are natural variables of internal energy because of how internal energy changes: $\partial U = T\partial S - P\partial V$; thus U(S,V). The conjugate variable of V is –P and the conjugate of S is T. In Sec. 3.3 we showed how to transform away internal energy's natural dependence on volume using a Legendre transform, whereby the natural variable times its conjugate $(-PV)$ are subtracted from the original function: $U-(-PV) = U+PV$ to create a new function with pressure as a natural variable. This can be verified by examination of the change in enthalpy: $\partial H = T\partial S + V\partial P$, from which we see that the natural variables of enthalpy are S and P.

Let's use a Legendre transform to take away internal energy's dependence on entropy and place it on temperature by subtracting S times its natural variable T. Let's call this new function the Helmholtz energy A:

$$A = U - TS \tag{5.1.1}$$

To determine the natural variables of A we calculate the differential of the Helmholtz energy:

$$\partial A = \partial U - \partial(TS) = -P\partial V + T\partial S - T\partial S - S\partial T = -P\partial V - S\partial T \tag{5.1.2}$$

Consequently, Helmholtz has natural variables of volume and temperature, i.e. A(V,T).

Let's take Helmholtz energy out for a ride like a stolen car to see what it can do. Recall that the change in U has the property of being the same as heat transferred so long as volume is held constant. The same is true for the change in H when the pressure is fixed. Both these facts are important because we power the planet with heat from burning things, including nuclear fuel. When we look at the change in A, it should become immediately apparent that when the temperature is constant then $\partial A = \partial w_{rev} = -P\partial V$. Thus, the change in A is the reversible work under conditions of constant temperature (its natural variable). In fact, the reason we use the letter "A" for Helmholtz energy is that it stands for "arbeit", which is German for work.

The next thing we want to show is that A is related to the total entropy change under the condition that both its natural variables (T and V) are held constant; see Sec. 4.2.1 if you forgot about how to relate energy to entropy via the Clausius inequality which is basically the 2^{nd} Law of Thermodynamics. Regardless, we will review everything here. The Clausius inequality stipulates that the change total entropy always increases or stays the same. It is expressed as the sum of the change in the system ∂S plus surrounding entropy:

$$\partial S - \frac{\partial q}{T} \geq 0\ J/K$$

where $-\frac{\partial q}{T}$ is the change in the surrounding's entropy. If we multiply the above by –T:

$$\partial q - T\partial S \leq 0\ J$$

This doesn't seem to take us anywhere, so next we will both subtract and add $S\partial T$ on the left side in hoped of finding ∂A in the equation:

$$\partial q - T\partial S - S\partial T + S\partial T \leq 0\ J \tag{5.1.3}$$

We have to take a small break to derive how the change in Helmholtz energy is related to heat. First note that:

$$\partial A = \partial U - \partial(TS) = \partial U - T\partial S - S\partial T$$

and since $\partial U = \partial q - P\partial V$:

$$\partial A = \partial q - P\partial V - T\partial S - S\partial T$$

Now if volume, a natural variable of A, is held constant, then:

$$\partial A = \partial q - T\partial S - S\partial T \tag{5.1.4}$$

And now we can insert ∂A from Equation 5.4 above into equation 5.3:

$$\partial A + S\partial T \leq 0\ J$$

Like before, we appear stuck until we remember that we must hold both of A's natural variables constant, which are V and T. Holding T constant means $\partial T = 0\ K$ and thus:

$$\partial A \leq 0\ J$$

Since this derivation began with $\partial S_{tot} \geq 0\ J/K$ (total entropy increases), the above is a statement of the exact same thing. Thus for a process to be spontaneous under conditions of constant volume and temperature then the Helmholtz energy must decrease.

Before moving on, we should consider chemical processes under constant volume. There are many examples, such as the cracking of hydrocarbons by the petroleum industry. Also the high temperature and pressure production of ammonia by the Haber-Bosch process, which is the catalytic reaction of hydrogen and nitrogen gases at 500 $^\circ$C and 200 atm. You may have felt a twinge in your stomach when you read this- sounds dangerous, right? You bet; a chemist must be extremely cautious about initiating a reaction under constant volume conditions. This is because if gas is evolved and the reaction becomes hot, the pressure of the vessel may rise uncontrollably until an explosion occurs. There is a solution to the problem- don't ever do chemical reactions in closed vessels, rather, keep the pressure constant. But now we need a new definition of energy which has pressure as a natural variable.

5.2: Gibbs Energy

Gibbs energy is the ultimate Legendre transform as we must remove both natural variables of internal energy (S and V) and put them on their conjugates, T and –P. Hopefully this is rather obvious at this point:

$$G = U + PV - TS \tag{5.2.1}$$

We can establish the natural variables by determining the change in the Gibbs energy function:

$$\partial G = \partial U + \partial (PV) - \partial (TS)$$

Since $\partial U = -P\partial V + T\partial S$, $\partial (PV) = P\partial V + V\partial P$, and $\partial (TS) = T\partial S + S\partial T$:

$$\partial G = -P\partial V + T\partial S + P\partial V + V\partial P - T\partial S - S\partial T$$

which simplifies to:

$$\partial G = V\partial P - S\partial T \tag{5.2.2}$$

We can derive Equation 5.6 faster if we started with enthalpy, since $H = U + PV$ and H already has P as a natural variable. We simply Legendre transform away enthalpy’s dependence on entropy:

$$G = H - TS \tag{5.2.3}$$

Taking the change of this function reveals:

$$\partial G = \partial H - \partial (TS) = V\partial P + S\partial T - T\partial S - S\partial T$$

which simplifies to Equation 5.6:

$$\partial G = V\partial P - S\partial T$$

Regardless of the approach we see that the natural variables of Gibbs energy are pressure and temperature, i.e. G(T,P).

As with Helmholtz energy, Gibb’s energy has special meanings when its natural variables are held constant. For instance, under constant temperature conditions $\partial G = V\partial P$. We expected ∂G to be reversible work, just like the change in Helmholtz energy at constant temperature, but that doesn’t appear to be the case. Or is it? To investigate further, first calculate the change in G with respect to V at constant T:

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{\partial P}{\partial V}\right)_T$$

If we insert the perfect gas law then:

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{-nRT}{V^2}\right) = V\left(\frac{-P}{V}\right) = -P$$

Since we can “juggle” the partials algebraically, we can bring ∂V to the right to show:

$$\partial G = -P\partial V = \partial w_{rev}$$

under constant temperature conditions. So, like Helmholtz energy, Gibbs energy is also reversible work at constant T.

Last, under consideration is at constant temperature and pressure a negative change in Gibbs energy is the same as a positive change in total entropy. This proof of spontaneity is left to you as a problem at the end of this chapter. Regardless, Gibbs energy is special because nearly all processes that occur in Nature are under constant temperature and pressure conditions. Note that we also told you in high school that only negative changes in Gibbs energy were spontaneous. This was a lie, because if we lived in a constant entropy and volume world you would have learned that only negative changes in internal energy define spontaneity.

5.3: Calculations- Numerical and Derivations

We now have 12 variables (U, P, V, T, ∂q, ∂w, H, C$_V$, C$_P$, S, A, and G) that can change via four distinct mechanisms (isothermal or adiabatic $\times$ reversible or irreversible). This lends itself to 48 types of thermodynamic calculations, although this is actually an over estimation because changes in state variables (U, H, A, G, S) are the same regardless of the condition due to exactness. We will now review methods to calculate ΔA and ΔG for gas expansion / contraction problems, although some problems don't have simple solutions. This chapter is also the last holdout for these types of pressure-volume questions, because in Chapter 6 and beyond we will apply thermodynamic calculations to chemical transformations.

5.3.1 Thermodynamic Calculations. We start with calculate changes in Gibbs and Helmholtz energies for gas pressure-volume transitions under isothermal and adiabatic conditions. The fact that G and A are state variables means that there are some generalities that make these problems easier. For example, the changes in Gibbs and Helmholtz energies for either reversible or irreversible isothermal transitions are both equal to the reversible work: $\partial A = \partial G = \partial w_{rev}$. Since we have discussed calculations of reversible work extensively in previous chapters, there isn't much else to say here!

The next two conditions are the reversible and irreversible adiabatic cases. Concerning the adiabatic reversible, the change in Gibbs energy is:

$$\partial G = \partial H - \partial(TS) = \partial H - S\partial T - T\partial S$$

and since the system entropy is constant ($\partial S = 0\ J/K$) and $\partial H = C_P\partial T$ under adiabatic reversible conditions:

$$\partial G = \partial H - S\partial T = C_P\partial T - S\partial T$$

Here we see that the change in Gibbs energy can be calculated once the change in temperature has been determined. Using the same procedure we can show:

$$\partial A = C_V\partial T - S\partial T$$

which also demonstrates the ability to calculate the change in Helmholtz energy with temperature. This requires that the absolute value of the entropy of the system (S) must be known, and it can be using the 3^{rd} Law of Thermodynamics as discussed in the next chapter. However, this is a bit complex so we won't consider this further.

Calculations of A and G for adiabatic irreversible transitions are problematic; consider for example:$partialG = \partial H - \partial(TS)$. Here, both S and T are simultaneously changing because entropy is a function of temperature. We encountered a similar problem with enthalpy: $\partial H = \partial U + \partial(PV)$, where the complicating $\partial(PV)$ term was resolved using the perfect gas law as: $\partial(PV) = nR\partial T$. However, we don't have a perfect gas law for entropy and temperature, and as such calculating the changes in Helmholtz and Gibbs energies for adiabatic irreversible transitions is not straightforward. We also question the value of knowing the changes of Gibbs and Helmholtz energies for adiabatic transitions because they do not represent total entropy and are not directly applicable towards determining the spontaneity of a process.

5.3.2 Pressure and Volume. Knowledge of Helmholtz and Gibbs energies allow us to examine more complex thermodynamic proofs. We have already established that $\left(\frac{\partial G}{\partial V}\right)_T = -P$, which means that the Gibbs energy of a substance goes down with increasing volume (–P can only be negative). What is more important is how Gibbs energy changes with pressure, its natural variable, at constant temperature. Beginning with $\partial G = V\partial P - S\partial T = V\partial P$, since $\partial T = 0\ K$, then $\left(\frac{\partial G}{\partial P}\right)_T = V$ which means that Gibbs energy always goes up with increasing pressure as volume is always positive. This probably doesn't sound interesting now, but it will be very important to understand phase diagrams later in Chapter 8. Examining how Helmholtz and Gibbs Energies change with temperature is a bit more complex as discussed below.

5.3.3 Temperature and the Gibbs-Helmholtz Equation. As stated at the beginning of this chapter, the Earth is best described as a constant temperature and pressure system. Under these conditions a negative change in Gibbs energy means that the total entropy of a process is increasing, which determines spontaneity. Thus, knowing how Gibbs energy changes with temperature is very important.

Some might ask why we concern ourselves with changes in Gibbs energy with temperature, when ΔG is related to spontaneity (increasing ΔS_{tot}) at constant temperature. It's because a chemical process can be conducted at constant temperature, but we never said at what temperature. For example, if a reaction is not spontaneous at 25 ºC, it might be if we changed the temperature (and then held the temperature constant). The way to know this is to determine $\left(\frac{\partial G}{\partial T}\right)_P$ starting with:

$$\partial G = V\partial P - S\partial T = -S\partial T$$

where we invoked constant pressure ($\partial P = 0\ Pa$), and after dividing both sides by ∂T we see: $\left(\frac{\partial G}{\partial T}\right)_P = -S$. Since entropy is always positive according to the 3^{rd} Law as described in Chapter 6, Gibbs energy goes down with increasing temperature in proportion to the entropy. This information gives us much insight- if the products of a reaction have greater entropy than the reactants, then increasing the temperature will likely result in a more negative ΔG which is good.

But now, there is a big problem in that there is no such thing as an entropy “thermometer”, and even worse entropy is a function of temperature. Thus, we need to try to replace entropy with something else to make the determination of $\left(\frac{\partial G}{\partial T}\right)_P = -S$ easier. Starting with $G = H - -TS$, we can see that \(S=\frac{H-G}{T}), which then gives us:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G-H}{T} \tag{5.3.1}$$

Here, we are mathematically “stuck” because we have ∂G on the left side of the equation and G on the right, and we have to have them both on the left side to do anything with Equation 5.8. Unfortunately there is no easy way to algebraically factor G out of $\frac{G-H}{T}$ on the right-hand side.

It turns out that we can simply change the question; rather than try to determine how G changes with T, instead we ask how G/T changes with T. This will work because temperature is always positive, and thus it won’t affect whether ∂G is positive (less spontaneous) or negative (more spontaneous) with increasing temperature. Let us start with:

$$\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = \frac{1}{T}\left(\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right) \tag{5.3.2}$$

which comes from the product rule: $\frac{\partial(f\cdot g)}{\partial x} = f\frac{\partial g}{\partial x} + g\frac{\partial f}{\partial x}$, where f=1/T, g=G, and x=T. Going back to equation 5.8: $\left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T}$ to which we make some rearrangements: $\left(\frac{\partial G}{\partial T}\right)_P = \frac{G}{T} - \frac{H}{T}$ we find that:

$$\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = -\frac{H}{T}$$

The above is inserted into Equation 5.9:

$$\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = \frac{1}{T}\left(\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T}\right) = \frac{1}{T}\left(-\frac{H}{T}\right) = -\frac{H}{T^2}$$

This is the Gibbs-Helmholtz equation, which will be very important in our further developments on phase transitions and colligative properties discussed in later chapters. For now, let’s use it to answer the original question as to whether we should heat up a chemical reaction that isn’t “going” (non-spontaneous) as it has a positive ΔG. For a reaction, we take the Gibbs-Helmholtz equation $\left(\frac{\partial \frac{G}{T}}{\partial T}\right)_P = -\frac{H}{T^2}$ and we re-write it in terms of changes of those thermodynamic functions:

$$\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P = -\frac{\Delta H}{T^2} \tag{5.3.3}$$

Next, an endothermic reaction has a positive ΔH, because enthalpy is heat at constant pressure and endothermic reactions soak in heat. Thus, $-\frac{\Delta H}{T^2}$ is negative and that makes $\left(\frac{\partial \frac{\Delta G}{T}}{\partial T}\right)_P$ negative too. Consequently, if we increase T, then $\frac{\Delta G}{T}$ (and thus ΔG)

becomes more negative, which is good for making a reaction spontaneous. We can also explain this using Le Chatelier’s principle. An endothermic reaction has heat as a reactant:

heat + reactants $\rightarrow$ products

and thus adding more heat by increasing the temperature should lead to more products. See, you knew this all the time! Last, if a reaction is exothermic, then you will want to cool the system because doing so lowers ΔG and increases the reaction’s spontaneity.

5.4: Advanced Derivations - Maxwell Relationships II

We had a brief introduction to Maxwell relationships in Sec. 4.5. In case you don't recall, a Maxwell relation is based on the Euler test for exactness of a partial function. For the change in a function (i.e., the differential):

$$\partial f = \left(\frac{\partial f}{\partial x}\right)_y \partial x + \left(\frac{\partial f}{\partial y}\right)_x \partial y$$

then if ∂f is exact partial differential: `\left( \dfrac{\partial }{\partial y}{\frac{\partial f}{\partial x} \right)_y)}_x=\left( \dfrac{\partial }{\partial x}{\frac{\partial f}{\partial y} \right)_x)}_y`. Since state variables (U, H, A, G, and S) have exact partials, we can use them to derive Maxwell relations with the Euler test. Starting with internal energy:

$$\partial U = T\partial S - P\partial V$$

therefore: `\left( \dfrac{\partial }{\partial V}{\frac{\partial U}{\partial S} \right)_V)}_S=\left( \dfrac{\partial }{\partial S}{\frac{\partial U}{\partial V} \right)_S)}_V` , and since $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$, then:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\partial P}{\partial S})_V \tag{5.4.1}$$

Likewise $\partial H = T\partial S + V\partial P$, which leads to `\left( \dfrac{\partial }{\partial P}{\frac{\partial H}{\partial S} \right)_P)}_S=\left( \dfrac{\partial }{\partial S}{\frac{\partial H}{\partial P} \right)_S)}_P` and thus:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{5.4.2}$$

These are the relationships derived from Ch. 4. More interesting relationships are derived from:

$\partial A = -S\partial T - P\partial V$ and $\partial G = -S\partial T + V\partial P$

such as:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{5.4.3}$$

and:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{5.4.4}$$

Equations 5.4.3 and 5.4.4 are especially useful for understanding changes in entropy, which tends to be a very difficult subject.

5.4.1 Using Maxwell Relations

Maxwell relations can reveal many thermodynamic principles, some we have seen already and some that we have not. For example, what can we do with the fact that $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ from Equation 5.11? The derivative on the right is easy to determine using the perfect gas equation: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial \frac{nRT}{V}}{\partial T} = \frac{nR}{V}$. Thus, $\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V}$ which is always positive as there is no such thing as negative values for n, R, and V. This means that increasing the volume of a perfect gas at constant temperature will increase the entropy. This makes sense because we previously derived the equation: $\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$ that demonstrates the same. In fact, we can re-derive this using: $\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V}$, which is rearranging as: $\partial S = \frac{nR}{V}\partial V$ and then integrated: $\int_{S_i}^{S_f} \partial S = \Delta S = \int_{V_i}^{V_f} \frac{nR}{V}\partial V = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$.

What if we had started with the Helmholtz Maxwell relation: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ from Equation 5.12? The derivative on the right is easy to determine using the perfect gas equation: $-\left(\frac{\partial V}{\partial T}\right)_P = -\frac{\partial \frac{nRT}{P}}{\partial T} = -\frac{nR}{P}$. Thus, $\left(\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P}$ which is always negative. This means that increasing the pressure of a perfect gas at constant temperature will lower the entropy. This makes sense because you must lower the gas's volume to increase pressure, which we already know will cause the entropy to drop. We can in fact determine the relationship between entropy and pressure changes using: $\left(\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P}$, which is rearranged as: $\partial S = -\frac{nR}{P}\partial P$ and then integrated: $\int_{S_i}^{S_f} \partial S = \Delta S = -\int_{P_i}^{P_f} \frac{nR}{P}\partial P = nR\cdot\ln\left(\frac{P_i}{P_f}\right)$. If we insert the perfect gas equation for the pressure we find $\Delta S = nR\cdot\ln\left(\frac{\frac{nRT}{V_i}}{\frac{nRT}{V_f}}\right) = nR\cdot\ln\left(\frac{V_f}{V_i}\right)$ as stated before.

5.4.2 Compressibilities

Maxwell relations allow us to understand the thermodynamics behind some measurable physical properties of materials, specifically the expansion coefficient $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. Specifically, we can show that $\left(\frac{\partial S}{\partial V}\right)_T$, $\left(\frac{\partial V}{\partial S}\right)_P$, $\left(\frac{\partial P}{\partial S}\right)_V$, and $\left(\frac{\partial S}{\partial P}\right)_T$ can all be expressed as functions of$alpha$ and κ_T using the Euler Chain formula $\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$, which rearranges to $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial x}{\partial z}\right)_y$.

$\left(\frac{\partial S}{\partial V}\right)_T$**.** Start with the Helmholtz Maxwell equation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. From there we use the Euler Chain Formula: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T$. Knowing that $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ and thus $\alpha V = \left(\frac{\partial V}{\partial T}\right)_P$ we can reduce the above to: $\left(\frac{\partial S}{\partial V}\right)_T = -\alpha V\left(\frac{\partial P}{\partial V}\right)_T$. We were given that: $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, which is rearranged as: $\frac{1}{\kappa_T} = -V\left(\frac{\partial P}{\partial V}\right)_T$ to yield the final result:

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa_T}$$

$\left(\frac{\partial V}{\partial S}\right)_P$**.** Starting with the enthalpy Maxwell equation $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$ and applying the Euler Chain Formula on the right side: $\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial T}{\partial S}\right)_P$. Knowing that $\partial H = T\partial S + V\partial P$, the partial with respect to T at constant P gives $C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$ and therefore $\frac{T}{C_P} = \left(\frac{\partial T}{\partial S}\right)_P$. Thus the Euler Chain formula above reduces to: $\left(\frac{\partial V}{\partial S}\right)_P = -\frac{T}{C_P}\frac{\partial S}{\partial P})_T$. To get rid of the entropy term we use the Gibbs energy Maxwell Equation $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$, which leaves us with: $\left(\frac{\partial V}{\partial S}\right)_P = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$. Knowing that $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ we can reduce this to:

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{TV\alpha}{C_P}$$

Conclusion

After nearly ∼100 pages and 5 chapters of Physical Chemistry I, you finally know all there is to know about how a gas expands and contracts. Congratulations! Now we move into the more practical aspects of thermodynamics, which are the energetics of chemical reactions. The greatest use of this science is the ability to accurately predict reaction yields, which is very useful for industry that produces chemicals on megaton-scales. However, we will now see how limited our understanding of energy is, and how we can at best only relatively understand thermodynamic principles of energy.

CHAPTER OVERVIEW

6: Chemical Thermodynamics

Thus far we have studied the thermodynamics of gases expanding or contracting. While this is important given how modern engines work, where's the chemistry? It's about time that we examine the thermodynamics of actual chemical reactions and other transformations, such as phase changes. Over the next few chapters we will show how thermodynamics can be used to calculate chemical reaction yields, the freezing temperature of water, and how both the freezing and boiling points of water are changed by salting it. To do so, we first have to define the energies and entropies of actual chemicals. This requires tabulating thermodynamic data on basically all known substances. To this end, you are undoubtedly familiar with calorimetry to measure enthalpy. Gibbs energy can then be derived from enthalpy by measuring the entropy. And in the next section we discuss how to measure entropy.

6.1: Entropy and the 3rd Law

Of all the thermodynamic variables, entropy is the only one that can be quantified with certainty due to the 3rd Law:

The absolute value of the entropy of a perfect crystal at 0 K is 0 J/K

A little dry, isn't it? What is important is that the 3rd Law gives us a starting point for measuring the entropy of a real chemical, that being a frozen, perfect crystal of the substance at 0 K. Next, the material is heated to room temperature, all the while constantly measuring how much energy is added. All this heat energy is translated into entropy using the various equations we developed in Chapter 4 and further here. We assume that we have 1 mole of a pure, perfectly crystalline chemical in a calorimeter. As we efficiently add heat, we must know whether the conditions are those of constant volume or pressure given that the heat capacity depends on these factors. As it isn't easy to keep a solid at a constant volume, we make these measurements at a constant pressure. Recalling that: $\partial q = C_P \partial T$, and assuming the heat is added reversibly: $\partial S = \frac{\partial q_{rev}}{T}$) , the absolute entropy is:

$$S\left(T_f\right) = S\left(0\ K\right) + \int_{T_i}^{T_f} C_P \frac{\partial T}{T} = S\left(0\ K\right) + C_P \cdot \ln\left(\frac{T_f}{T_i}\right)$$

where $S\left(0\ K\right)$ is 0 J/K due to the 3rd Law. From this, can you can see how the 3rd Law allows us to determine the actual entropy of a chemical is at room temperature and pressure? If we didn't know $S\left(0\ K\right)$, then we could never calculate the absolute value of S at any temperature!

As an example, we will determine the entropy of nitrogen gas at 25 $^\circ$C starting from 0 K. First, you may be tempted to use the value of $C_{P,m}$ that we determined in Chapter 2: $C_{P,m} = C_{V,m} + R = \frac{5}{2}R + R = 29.1\ J/K/mol$. The problem is that this is the per molar heat capacity of N_2 gas near room temperature, not the heat capacity of solid nitrogen near 0 K! These heat capacities are not the same, in fact, they are very different as heat capacity of N_2 is dependent on both the phase and temperature as shown in Figure 6.1A. We can see that the per molar heat capacity of the solid at ∼0 K is ∼0 J/K/mol, and quickly rises with temperature until T = ∼36 K. Next the heat capacity suddenly decreases, which is due to a solid-solid phase transition. What this means is that N_2 remains a solid, but the internal structure changes from cubic to hexagonal close-packed. This is still a change of phase, just like ice melting into water. There is also an associated heat of transition per mole, $\Delta_{h\leftarrow c}H_m$, which is the energy added to 1 mole of N_2 in the cubic phase to transform it into a hexagonal solid ("$h \leftarrow c$" refers to the solid phase transition from cubic to hexagonal). Since the addition of heat will always increase entropy, this must be added in as:

\[S_m=S_m\left(0\ K\right)+C_{P,m}\left(T\right)\cdot \ln \left(\frac{T_{h\leftarrow c}}{T_i}\right)+\frac

ParseError: invalid DekiScript (click for details)

\nonumber \]

where $T_{h\leftarrow c}$ is the temperature at which this phase change occurs (∼36 K). Next, we heat the hexagonal solid phase of nitrogen to 63 K, at which point the N_2 begins to melt. As before, the head added to allow this phase transition to occur increases the entropy and is added to the total:\(S_m=S_m\left(0\ K\right)+C_{P,m}\left(T\right)\cdot \ln \left(\frac{T_{h\leftarrow c}}{T_i}\right)+\frac

ParseError: invalid DekiScript (click for details)

+C_{P,m}\left(T\right)\cdot \ln \left(\frac{T_{fus}}{T_{h\leftarrow c}}\right)+\frac

ParseError: invalid DekiScript (click for details)

\)

where "fus" is fusion (the IUPAC word for melting) and T_{fus} is the melting temperature (∼64 K). We repeat this process using additional terms to account for warming the liquid to the vaporization temperature, and then vaporizing to liquid to form a gas, etc., until we reach 298.15 K:

\[S_m(298.15\ K)=S_m\left(0\ K\right)+C_{P,m}\left(T\right)\cdot \ln \left(\frac{T_{h\leftarrow c}}{T_i}\right)+\frac

ParseError: invalid DekiScript (click for details)

+C_{P,m}\left(T\right)\cdot \ln \left(\frac{T_{fus}}{T_{h\leftarrow c}}\right)+\frac

ParseError: invalid DekiScript (click for details)

+C_{P,m}\left(T\right)\cdot \ln \left(\frac{T_{vap}}{T_{fus}}\right)+\frac

ParseError: invalid DekiScript (click for details)

+C_{P,m}\left(T\right)\cdot \ln \left(\frac{298.15\ K}{T_{vap}}\right) \label{6.1}\]

When we do this calculation using the $C_{P,m}(T)$ data shown in Figure 6.1A, including the enthalpies of all the various phase transformations, we determine that 1 mole of gaseous N_2 at this temperature and 1 bar of pressure has 190.1 J/K of entropy. This value then gets placed in standard thermodynamic tables along with the data on every other chemical that has been measured the same way.

6.1.1Standard Temperature and Pressure

The above example demonstrates that thermodynamic values depend on the conditions at which they are reported. In the example above entropy is always increasing with temperature. Thus, we must designate a single, standard temperature (such as room temperature) that we use at the stopping point for the calculation in Equation 6.1. If we need to know the thermodynamic data at a different temperature, we can simply take the value from this standard state and then adjust it appropriately. This happens frequently, and we will show how to do so later in this chapter.

Before we get ahead of ourselves, we must define the standard state at which all thermodynamic data are tabulated. Furthermore, we have to define what variables comprise the standard state! To this end, we use pressure and temperature because these are intensive variables, and intensive variables are the deciding factors that determine equilibrium (this is explored in Chapter 8). For example, water and ice at equilibrium have the same temperature at the same pressure, whereas they do not have the same entropy and volume. Thus, we choose to define the standard state using temperature and pressure; specifically at 25 ºC (298.15 K) and 1 bar (100 kPa).**6.2 Energy, it’s all relative. 6.3 Enthalpy and Gibbs Energy of Formation: Hess’s Law examples.**

6.2: Energy, it’s all relative

Now that we can calculate the entropy per mole of all chemicals at the standard state, we would like to tabulate it with the Gibbs energy per mole as derived from the enthalpy using: $G_m = H_m - (298\ K \times S_m)$. From there we could evaluate whether any reaction was spontaneous without having to go to a lab, put all the chemicals in a reactor and measure the reaction yields etc. All we do is get the sum of the G_m’s of the reactants and subtract that from the sum of the same of the products. Given the equations above, all we need to know is the absolute enthalpy per mole H_m that we can be determine using $H_m = U_m + PV$.

Unfortunately there is a terrible problem; we need to know U_m but there is no 3^{rd} Law for the absolute internal energy. This is probably confusing because it appeared we defined the internal energy in Chapter 2 via the Equipartition theorem: $U_m = \frac{1}{2}RT \cdot (degrees\ of\ freedom)$. The Equipartition theorem relates the internal energy to the temperature of a chemical, but now we have to ask, *what kind of energy?* In Chapter 2, we were considering gas molecules’ ability to translate through space; maybe it could rotate as well. These types of energies were important because it helped us determine the work done by an expanding piston. What this definition of U_m ***does not do*** is allow us to determine the energy of a gas molecule if it reacts with another. Reactions are dependent on bond breaking and making, which has to do with the arrangement of electrons between the atoms. And the energy of electrons must depend on their own degrees of freedom, which is difficult to think about because electrons are very light and behave via the rules of quantum mechanics. For example, do electrons in the \sigmaup-bonds of hexane have more or less degrees of freedom of those in the delocalized \piup-bonds of benzene? And if so, how do you use that information to calculate the internal energy?

At this point, you are probably confused about energy, and so are the authors of this book! In fact, it is difficult to know whether absolute energy even exists when all we do is measure changes in energy. However, perhaps such knowledge of relative energies is good enough for us to predict the thermodynamics and yields of chemical reactions, which is all that chemists care about anyways. This is in fact true and the subject of the next section.

6.2.1 Hess’s Law and the Gibbs Energy of Chemical Reactions. Let’s consider some chemical reactions related to home fuels. In terms of household heating, one good use of thermochemistry would be to discover a reaction that produces a lot of heat via a large negative enthalpy ($\Delta_r H^\circ$, where “r” means “reaction” and $^\circ$ means the value was measured at the standard state T=298.15 K and P = 100 kPa). Burning propane is a good example:

1 $CH_3CH_2CH_3(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$ $\Delta_r H^\circ$ = -2219.2 kJ

but we see a lot of “bad” carbon dioxide produced. Perhaps there is another reaction that produces heat without as much $CO_2(g)$? To do so, let’s tabulate the $\Delta_r H^\circ$’s of all possible chemical reactions and sort them based on exothermicity. We can do this by adding the reactants’ enthalpies and subtract that from the sum of the products’ enthalpies. However, knowledge of a chemical’s absolute enthalpy content is not possible as we just discussed. And with no ability to make predictions, we are going to have to experimentally measure all the enthalpies of all reactions that could ever exist. While the results will be very accurate, this effort will take a huge amount of time and money.

It turns out that we can predict the enthalpies of chemical reactions without actually setting them off; we will demonstrate how this works with some examples. For example, the heat generated from the combustion of dimethyl ether is:

$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$ $\Delta_r H^\circ$ = -1460.4 kJ

This reaction produces a lot heat but less CO_2 than propane. Dimethyl ether is easier to transport than propane because is liquefies under mild conditions; perhaps we should use it instead of propane for a home fuel? Let’s also examine ethanol. Here we see that ethanol combustion is not as exothermic as dimethyl ether:

$CH_3CH_2OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$ $\Delta_r H^\circ$ = -1367.0 kJ

but it is a “green” fuel because ethanol can be produced by fermentation, which is a renewable process. Ethanol can also be synthesized from dimethyl ether:

$CH_3OCH_3(g) \rightarrow CH_3CH_2OH(l)$ $\Delta_r H^\circ$ = -93.4 kJ

Now here is an important observation- the difference in the enthalpy of combustion of dimethyl ether and ethanol:

-1460.4 kJ – -1367.0 kJ = -93.4 kJ

just happens to be the same as the difference in enthalpy of forming ethanol from dimethyl ether shown above! It’s as though we can combine the reactions as though they are equations. If this statement is confusing, let us demonstrate exactly what we mean by summing the combustion reaction of diethyl ether with the reverse reaction of the combustion of ethanol:

$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)$ $\Delta_r H^\circ$ = -1460.4 kJ

+

$\Delta_r H^\circ$

The result is:

$3\ H_2O(l){+}CH_3OCH_3(g){+}3O_2(g){+}\ 2CO_2(g){\rightarrow}2CO_2(g){+}3H_2O(l){+}CH_3CH_2OH(g){+}3O_2(g)$

The enthalpy ($\Delta_r H^\circ$) of the combustion reaction of ethanol was switched from negative to positive because the reaction is written in reverse. Next, there are identical species (oxygen, water, and carbon dioxide) on the right and left of the net reaction that can be removed because they don't "do" anything if they are on both sides of the equation. This simplification yields:

$3\ H_2O(l){+}CH_3OCH_3(g)\ 3\ H_2O(l){+}3O_2(g){+}2CO_2(g){\rightarrow}2CO_2(g){+}3H_2O(l){+}CH_3CH_2OH(l){+}3O_2(g)$

The leftovers are:

$CH_3OCH_3(g) \rightarrow CH_3CH_2OH(l)$ $\Delta_r H^\circ$ = -93.4 kJ

These are summarized in Figure 6.2, where we can see that the difference in the enthalpy of the combustion reaction of dimethyl ether and ethanol is the same as the enthalpy difference between forming ethanol from diethyl ether. The combination of all these data form a thermodynamic cycle, which means that we can generate new data on reactions that we haven't actually measured so long as it closes a cycle of other reactions with known thermochemistry.

One more example; let's see what happens if we burn dimethyl ether such that the product is steam (i.e. gaseous water, see Figure 6.3):

$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O$**(g)** $\Delta_r H^\circ$ = -1328.4 kJ

Compared to our previous example that had liquid water as a product, we can use these data to determine $3\times$ the enthalpy of vaporization of water:

-1328.4 kJ/mol – -1460.4 kJ/mol = 132.0 kJ/mol

(the factor of $3\times$ exists because there are three moles of water formed in this reaction). For 1 mol of water this is +44.0 kJ/mol. In fact, if we Google the enthalpy of vaporization of water we quickly discover the same value: +40.0 kJ/mol! Note that this also shows that we must be careful when we do Hess's Law problems that we have to pay attention to the phases of the chemicals in the reaction.

We have covered several specific examples thus far, and maybe it's a bit confusing as to how we are performing these manipulations. So instead let's study some examples for summing chemical reactions for which we will use labels like "A" & "B" etc. for the reactants and products:

A + B $\rightarrow$ C + D $\Delta_r H^\circ$ = X kJ

+

\(\Delta_rH{}^\circ)

A + B + C + D $\rightarrow$ C + D + F + G $\Delta_r H^\circ$ = (X + Y) kJ

We simply add the chemicals to the left of the "$\rightarrow$" sign together, and ditto for the right side. Likewise we add the enthalpies together. In the net reaction at the bottom we can eliminate C and D since they are on both sides: A + B + C + D $\rightarrow$ C + D + F + G, leaving:

A + B $\rightarrow$ F + G $\Delta_r H^\circ$ = (X + Y) kJ

What this example demonstrates is a process that can be applied to calculate the enthalpy for the reaction A + B $\rightarrow$ F + G.

Here is a more difficult example. If we are looking to calculate the enthalpy for the reaction A + B $\rightarrow$ F + G using the following:

A + B $\rightarrow$ 2C + 2D $\Delta_r H^\circ$ = X kJ

+

½ F + ½ G $\rightarrow$ C + D $\Delta_r H^\circ$ = Y kJ

This is more difficult because we can't directly add these equations together. In fact, we need to reverse the second reaction and then multiply it by 2×, and then we can sum the two to get the correct reaction stoichiometry (products, reactants, and relative number of moles). Note that the enthalpy is thus multiplied by -2×, where the minus comes about from reversing the reaction:

2C + 2D $\rightarrow$ F + G $\Delta_r H^\circ$ = -2×Y kJ

+

$\Delta_r H^\circ$

A + B + 2C + 2D $\rightarrow$ 2C + 2D + F + G $\Delta_r H^\circ$ = (X – 2×Y) kJ

As in the last example we eliminate the species that appear on both left and right sided to yield: A + B $\rightarrow$ F + G $\Delta_r H^\circ$ = (X – 2 ×Y) kJ

6.2.2 A reaction basis set. Let us not forget our end goal, which is to tabulate the enthalpy and Gibbs energy of chemical substances to predict the outcomes of reactions without necessarily having to actually measure them. To meet this goal, we first note that in every example above species "C" and "D" were ultimately removed. What if "C" is CO_2 and "D" is H_2O, which are always to one side of a combustion reaction? If so, then we can derive the thermochemistry of the reaction A + B $\rightarrow$ F + G solely using data from combustion reactions. Consequently, if we simply measure the thermochemistry of combusting every chemical we can get our hands on, the data derived from this effort can be mixed and matched as above to determine new thermochemical data for other types of reactions! So, some investment must be made to form a "basis set" of thermochemical combustion data, but that data ultimately produces savings when we want to predict the outcome of other reactions that aren't necessarily related to burning organic compounds.

6.2.3 Standard state. The approach outlined above for tabulating thermochemical data from a basis set of combustion reactions for all known chemical substances is a good idea and it can work, except for the fact that not all chemicals react with oxygen, i.e. they don't combust. And for those that do, we need to know the thermochemistry of combustion at exactly 1 bar and 298.15K (standard pressure and temperature). As burning things tends to generate a lot of heat and pressure, there is a bit of a problem here.

To summarize, the idea of tabulating data using a basis set of a particular reaction type is good, but we just have to pick something other than combustion. In this regard there is one reaction that all chemicals must participate in, *which is their own formation*. For example, dimethyl ether can be created from carbon, oxygen, and hydrogen because it is composed of those elements. Ditto for ethanol; and note that the carbon would likely be in the form of graphite since graphite is the most thermodynamically stable form of carbon. Likewise, oxygen and hydrogen are naturally found as gases. Here are examples of such data for dimethyl ether:

2 C(s,graphite) + ½ O_2(g) + 3 H_2(g) $\rightarrow$ CH_3OCH_3(g) $\Delta_f H_m^\circ$ = -184.1 kJ/mol

and for ethanol:

2 C(s,graphite) + ½ O_2(g) + 3 H_2(g) $\rightarrow$ CH_3CH_2OH(l) $\Delta_f H_m^\circ$ = -277.69 kJ/mol

Here we see some new symbols and units for these formation energies. For one, these data are per molar quantities since they are defined by the formation of one mole of dimethyl ether and ethanol. This is why you see the symbol "H_m°" as opposed to "H°" from the previous examples. We also use a subscript "f" for "formation" as opposed to "r" for "reaction". As previously, the ° means standard temperature and pressure.

The enthalpy difference between dimethyl ether and ethanol can be determined by reversing the dimethyl ether reaction and adding it to the formation reaction of ethanol:

CH_3OCH_3(g) $\rightarrow$ 2 C(s,graphite) + ½ O_2(g) + 3 H_2(g) \({-\Delta }_fH{}^\circ)= 1 mol × -184.1 kJ/mol

+

$\Delta_f H^\circ$

CH_3OCH_3(g)+2C(s,graphite)+½O_2(g)+3H_2(g) $\rightarrow$ CH_3CH_2OH(l)+2C(s,graphite)+½O_2(g)+3H_2(g)

After removing the redundant species that appear on both sides of the equation:

CH_3OCH_3(g) $\rightarrow$ CH_3CH_2OH(l) Δ_rH = 184.1 kJ + -277.69 kJ = -93.6 kJ

There! We calculated the enthalpy difference between ethanol and dimethyl ether by subtraction of their enthalpies of formation, albeit after some manipulation. We had to multiply the enthalpies of formation by the corresponding number of moles, which is because enthalpy is energy and energy is extensive. There is a slight difference with the result above (-93.6 kJ) from that calculated using combustion data (-93.4 kJ) in our previous example. This is common, and results from experimental errors, the source of your data, and rounding errors. Table 6.1 has more thermodynamic data that we will be using to work more examples below; more extensive thermodynamic tables can be found in a CRC or on-line.

Material	S°_m (J/K/mol)	$\Delta_f G^\circ_m$ (kJ/mol)	$\Delta_f H^\circ_m$ (kJ/mol)	$C^\circ_{P,m}$ (J/K/mol)
C (s,graphite)	5.74	0.0	0.0	8.64
CO(g)	197.674	-137.168	-110.525	29.14
CO_2(g)	213.74	-394.359	-393.509	37.1
CH_4(g)	186.264	-50.72	-74.81	35.31
$CH_3CHO_{(g)}$	250.3	-128.9	-199.2	57.3
CH_3OCH_3(g)	342.2	-135.2	-184.1	65.57
CH_3CH_2OH(l)	160.7	-174.78	-277.69	112.3
H_2O(g)	188.825	-228.572	-241.818	33.58
H_2O(l)	69.91	-237.129	-285.83	75.28
H_2(g)	130.684	0.0	0.0	28.64
N_2(g)	191.61	0.0	0.0	29.1
NH_3(g)	192.5	-16.45	-46.11	35.06
$(NH_2)_2CO$(s)	104.3	-197.4	-333.1	92.8
O_2(g)	205.138	0.0	0.0	29.41

There are some important data points to note in Table 6.1, such as the fact that the Gibbs energy and enthalpy of C(s,graphite), O_2(g), and H_2(g) are 0.0 k/mol. This is because no energy is required to form these species starting from themselves, as these are elements in their standard states. Some elements can be found in different forms, called allotropes, and all but the ground state must have non-zero formation energies. For example, diamond is made of pure carbon, but it is not the ground state and requires $\Delta_f H^\circ_m$ = 1.86 kJ/mol to be formed from graphite. Of course, everything including elements in their standard states still have finite values of entropy and heat capacity because these are absolute quantities and are not relative to their formation. Recall we demonstrated this when we calculated the entropy of N_2 gas at the standard state at the beginning of this chapter. In the next section we will demonstrate how to use the data in Table 6.1 starting with the calculation of the thermochemistry of combustion of dimethyl ether.

6.3: Enthalpy and Gibbs Energy of Formation- Hess’s Law examples

Given that the basis set of formation reactions can be used to calculate the thermodynamic data on any conceivable chemical transformation, we will now work several examples starting with the combustion reaction of dimethyl ether:

$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l)\ \Delta_r H^\circ$ = -1460.4 kJ

The reaction enthalpy is determined from:

$$\Delta_r H^\circ = \sum_{products} \upsilon \cdot \Delta_f H_m^\diamond - \sum_{reactants} \upsilon \cdot \Delta_f H_m^\diamond \tag{6.3.1}$$

Likewise:

$$\Delta_r G^\circ = \sum_{products} \upsilon \cdot \Delta_f G_m^\diamond - \sum_{reactants} \upsilon \cdot \Delta_f G_m^\diamond\ (6.3)$$

$$= \sum_{products} \upsilon \cdot \left(\Delta_f H_m^\diamond - T\Delta_f S_m^\diamond\right) - \sum_{reactants} \upsilon \cdot \left(\Delta_f H_m^\diamond - T\Delta_f S_m^\diamond\right) \tag{6.3.2}$$

where υ is the stoichiometric number of moles that each species contributes to the reaction and the symbol ° means that the data are measured under standard conditions (25 °C and 1 bar pressure). These equations comprise Hess’s Law, which is really just a restatement that energy is conserved (also known as the 1^{st} Law of Thermodynamics).

Back to task- we can determine the enthalpy of burning dimethyl ether by summation of the formation enthalpies of 3 mol×water and 2 mol×carbon dioxide minus the same for 3 mol×oxygen and 1 mol×dimethyl ether:

$$\Delta_r H^\circ = \sum_{products} \upsilon \cdot \Delta_f H_m^\diamond - \sum_{reactants} \upsilon \cdot \Delta_f H_m^\diamond = 3\ mol \times -285.83 \frac{kJ}{mol} + 2\ mol \times -393.509 \frac{kJ}{mol} - 3 mol \times 0.0 \frac{kJ}{mol} - 1\ mol \times 184.1 \frac{kJ}{mol} = -1460.4\ kJ/mol$$

and:

$$\Delta_r G^\circ = \sum_{products} \upsilon \cdot \Delta_f G_m^\diamond - \sum_{reactants} \upsilon \cdot \Delta_f G_m^\diamond = 3\ mol \times -237.129 \frac{kJ}{mol} + 2\ mol \times -394.359 \frac{kJ}{mol} - 3 mol \times 0.0 \frac{kJ}{mol} - 1\ mol \times 135.2 \frac{kJ}{mol} = -1364.9\ kJ/mol$$

Note that $\Delta_r G^\circ$ could have been calculated from the enthalpies and entropies as:

$$\Delta_r G^\circ = \sum_{products} \upsilon \cdot \left(\Delta_f H_m^\diamond - T \times \Delta_f S_m^\diamond\right) - \sum_{reactants} \upsilon \cdot \left(\Delta_f H_m^\diamond - T \times \Delta_f S_m^\diamond\right)$$

For example, take the thermochemical data on dimethyl ether:

Material	$S_m^\diamond$ (J/K/mol)	$\Delta_f G_m^\circ$ (kJ/mol)	$\Delta_f H_m^\circ$ (kJ/mol)	$C_{P,m}^\circ$ (J/K/mol)
$CH_3OCH_3(g)$	342.2	-135.2	-184.1	65.57

From this we can get $\Delta_f G_m^\diamond$ from $\Delta_f H_m^\circ$ = -184.1 kJ/mol and $S_m{}^\circ$ = 342.2 J/K/mol, which is:

$$-184.1 \frac{kJ}{mol} - -298.15 K \times 0.3422 \frac{kJ}{K \cdot mol} = -286.12 \frac{kJ}{mol}$$

Wait! Something is wrong, this isn’t the same molar Gibbs formation energy as in the table ($\Delta_f G_m^\diamond$ = -135.2 kJ/mol)! If we retrace our steps we can see that this incorrect result comes about from trying to calculate $\Delta_f G_m^\diamond = \Delta_f H_m^\diamond - T^\circ \times S_m^\diamond$, whereas we should have been using: $\Delta_f G_m^\diamond = \Delta_f H_m^\diamond - T^\circ \times \Delta_f S_m^\diamond$. The former, incorrect equation is using $S_m^\diamond$, but we should instead have calculated $\Delta_f S_m^\diamond$ for dimethyl ether using the entropy data for carbon, hydrogen and oxygen. From Table 6-1 this is the entropy of the following reaction:

2 C(s,graphite) + ½ $O_2(g) + 3\ H_2(g) \rightarrow CH_3OCH_3(g)$

which is:

$$1mol\times 342\frac{J}{K\cdot mol}-2mol\times 5.74\frac{J}{K\cdot mol}--½mol\times 205.14\frac{J}{K\cdot mol}--3mol\times 130.68\frac{J}{K\cdot mol}=-164.09 fracJK$$

Since this is the entropy for forming 1 mol of dimethyl ether from its elements in their standard states, we can state that this is the per molar entropy of formation $\Delta_f S_m^\diamond = -164.09\ J/K/mol$. When we use entropy properly we see that the data table is self-consistent:

$$\Delta_f G_m^\circ = \Delta_f H_m^\diamond - T^\circ \times \Delta_f S_m^\diamond = -184.1\frac{kJ}{mol} - -298.15\ K\times -0.16409\frac{kJ}{K\cdot mol} = -135.2\frac{kJ}{mol}$$

The exercise above demonstrates that our understanding of how Gibbs energy is related to enthalpy and entropy is correct. However, we don't recommend going through all of these calculations for the Gibbs energy if a table of $\Delta_f G_m^\circ$'s is already available!

The examples above allowed us to calculate thermodynamic data a variety of ways using Hess's Law. It must be noted that the results are only applicable to a reaction performed at room temperature and 1 bar pressure. You should know from your lab experiences that we often heat reactions (and in more advanced labs you sometime cool them!); how do you go about calculating thermodynamic values when you are no longer at the standard state? This is the subject of the next section on Kirchoff's Law.

6.3.1 Non-standard state reactions and Kirchoff's Law. Not all chemical reactions will occur at exactly 1 bar pressure and 25 ºC if they are not spontaneous. And of course you know that "not spontaneous" means $\Delta_r G^\circ\left(298\ K\right) > 0\ J$, which also means that total entropy does not increase as required by the 2^{nd} Law. Our intuition also tells us that heating a chemical reaction to a higher temperature T_2 will often make it "go", i.e., become spontaneous, which means $\Delta_r G\left(T_2\right) < 0\ J$ at this higher temperature. As a result, we often must adjust our thermochemical data for conditions other than the standard state. Here we will focus on temperature, starting with the relationships we derived in Chapter 3 for the temperature dependence of enthalpy:

$$\partial H = \partial U + \partial\left(PV\right) = \partial U + nR\partial T = C_v\partial T + nR\partial T = \left(C_v + nR\right)\partial T = C_P\partial T$$

While it is tempting to simply integrate the above to yield $\Delta H = C_P\Delta T$, this is an oversimplification. This is because when we integrate we need to know the upper and lower limits. Since we are adjusting the standard state thermochemical data from Table 6.1 the lower limit should be the standard temperature T° = 25 ºC = 298.15 K. The upper limit is the temperature at which we need to know the enthalpy; we will call T_2. Let's not forget that we need to do everything on a per molar basis as well. Thus:

$$\int_{\Delta_f H_m^\circ}^{\Delta_f H_m(T_2)} \partial\Delta_f H_m = \Delta_f H_m\left(T_2\right) - \Delta_f H_m^\circ\left(298.15K\right)$$

likewise:

$$\int_{T^\circ = 298.15K}^{T_2} C_{P,m}\partial T = C_{P,m}\left(T_2 - 298.15K\right)$$

assuming that the heat capacity is not temperature dependent which is not fully correct. Since the above are equal, $\Delta_f H_m\left(T_2\right) - \Delta_f H_m^\circ\left(298.15K\right) = C_{P,m}\left(T_2 - 298.15K\right)$, we can find $\Delta_f H_m\left(T_2\right)$:

\Delta_fH_m\left(T_2\right)=\Delta_fH^{{}^\circ }_m\left(298.15K\right)+C_{P,m}\left(T_2-298.15K\right) left(6.5\right) \nonumber

Using Equation 6.5 we can calculate the formation enthalpy at a new temperature for a single chemical substance, we then determine the same for all the participants in the reaction and then use these data as part of a normal Hess's Law calculation:

$$\Delta_r H\left(T_2\right) = \sum_{products} \upsilon\cdot\Delta_f H_m\left(T_2\right) - \sum_{reactants} \upsilon\cdot\Delta_f H_m\left(T_2\right)$$

Recall that our goal is to determine the change in Gibbs Energy, and for this we must determine how the absolute entropy of a chemical changes with temperature. As we already discussed how to adjust the entropy as temperature increases in Sec. 6.1, which we will adapt here starting at the standard state temperature:

$$S_m\left(T_2\right) = S_m^\circ + C_{P,m}\times\ln\left(\frac{T_2}{T^\circ = 298.15K}\right)\ (6.6)$$

With the knowledge of the proper entropy change of every chemical species in the reaction, the net entropy change is thus: $\Delta_r S = \sum_{products} \upsilon \cdot S_m (T_2) - \sum_{reactants} \upsilon{\cdot}S_m (T_2)$. Combined with the enthalpy change we now know: $\Delta_r G (T_2) = \Delta_r H (T_2) - T_2 \times \Delta_r S (T_2)$.

You may have noticed that these calculations are extremely tedious. However, there is a time-saving method to perform this calculation called Kirchoff's Law. First, note that the heat capacity is used to alter the enthalpy and entropy of each species individually. What if we calculate the reaction difference in heat capacities in the usual manner- products minus reactants:

$$\Delta_r C_P^\circ = \sum_{products} \upsilon{\cdot}C_{P,m}^\circ - \sum_{reactants} \upsilon{\cdot}C_{P,m}^\circ$$

and then use that to determine the reaction enthalpy at temperature T_2:
________,________,

$$\Delta_r H (T_2) = \Delta_r H^\circ (298.15 K) + \Delta_r C_P^\circ \times (T_2 - 298.15 K)$$

Likewise, the change in the reaction entropy at T_2:

$$\Delta_r S (T_2) = \Delta_r S_m^\circ (298.15 K) + \Delta_r C_P^\circ \times \ln\left(\frac{T_2}{298.15 K}\right)$$

to give us the change in Gibbs Energy at temperature T_2:

$$\Delta_r G (T_2) = \Delta_{\,r} H (T_2) - T_2 \times \Delta_r S (T_2)$$

This is the exact same thing as adjusting for the individual species' $\Delta_f H_m$ and S_m based on temperature, but faster as the example problems 6.1 & 6.2 illustrate.

6.3.2 Gibbs-Helmholtz approach. In example problems 6.1 & 6.2 we demonstrated examples of chemical reactions that require an increase the temperature to lower $\Delta_r G$. How could we have known this would work before going through all that tortuous calculator work? After all, maybe we needed to cool the reactions! To this end we can use a derivate of the Gibbs-Helmholtz relation, Equation 5.10 that we learned in Chapter 5:

$$\left(\frac{\partial\left(\frac{\Delta_r G}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_r H}{T^2} \tag{6.3.3}$$

From this we can immediately see that, if $\Delta_r H$ is positive (the reaction is endothermic), then the derivative $\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_P$ is negative. Thus, if the temperature increases (∂T is positive), then $\partial\left(\frac{\Delta G}{T}\right)$ is negative. And since T itself is positive, then a negative $\partial\left(\frac{\Delta G}{T}\right)$ requires that ΔG decreases. To summarize, ΔG decreases with increasing temperature for endothermic reactions, and of course ΔG increases with increasing temperature for exothermic reactions. We can make this clearer if we integrate the Gibbs-Helmholtz equation $\partial\left(\frac{\Delta G}{T}\right) = -\frac{\Delta_r H^\circ}{T^2}\partial T$ as shown here:

$$\int_{\frac{\Delta_r G^\circ}{T^\circ = 298.15\ K}}^{\frac{\Delta_r G(T_2)}{T_2}} \partial\left(\frac{\Delta_r G}{T}\right) = \int_{T^\circ = 298.15\ K}^{T_2} \frac{-\Delta_r H^\circ}{T^2}\partial T$$

where we assume the lower limit is the standard state temperature. The quantity we are trying to calculate, $\Delta_r G (T_2)$, is in the upper limit of the left-hand integral. Solving for it yields:

$$\frac{\Delta_r G (T_2)}{T_2} - \frac{\Delta_r G^\circ}{298.15\ K} = \Delta_r H^\circ \left(\frac{1}{T_2} - \frac{1}{298.15\ K}\right)$$

which simplifies to:

$$\Delta_r G (T_2) = \Delta_r H^\circ + \frac{(\Delta_r G^\circ - \Delta_r H^\circ) \times T_2}{298.15\ K} (6.8)$$

This equation looks a lot easier to work with than the calculations in example problems 6.1 & 6.2! In fact, if we plug in values for the steam forming reaction into the above, we find that $\Delta_r G\left(T_2\right)=0\ kJ$ at a temperature of 960 K (686.8 ºC). This is close, *but not identical*, to the result from the example problem which was 606.3 ºC. Why is that? If we insert the fact that $\Delta_r G^{\circ}=\Delta_r H^{\circ}-298.15K \times \Delta_r S^{\circ}$ into Equation 6.8 above then we can show that:

$$\Delta_r G\left(T_2\right)=\Delta_r H^{\circ}-T_2 \times \Delta_r S^{\circ}$$

This result is rather trivial as it is simply the standard state Gibbs energy: $\Delta_r G^{\circ}=\Delta_r H^{\circ}-T^{\circ} \times \Delta_r S^{\circ}$, where T° = 298.15 K, with a non-standard temperature T_2 inserted for T°. While solving Equation 6.8 is much easier than using Kirchoff's Law as in the example problems of the previous section, it clearly cannot be as accurate.

Where did we go wrong? A simplification must have been made when we integrated the Gibbs-Helmholtz equation, but where? A clue comes from the fact that Equation 6.8 doesn't incorporate the reaction heat capacity ($\Delta_r C_P^{\circ}$) to adjust the enthalpy for a non-standard temperature. In other words, the temperature dependence of $\Delta_r H$ was ignored when solving the $\int_{T_1=298.15\ K}^{T_2} \frac{-\Delta_r H^{\circ}}{T^2} \partial T$ integral. We treaded the enthalpy as temperature-independent, which is not very accurate. To resolve, we can add in the temperature dependence of enthalpy when solving the integral as:

$$\int_{\frac{\Delta_r G^{\circ}}{T^{\circ}=298.15\ K}}^{\frac{\Delta_r G\left(T_2\right)}{T_2}} \partial\left(\frac{\Delta_r G}{T}\right)=\int_{T^{\circ}=298.15\ K}^{T_2} \frac{-\left(\Delta_r H^{\circ}+\Delta_r C_P^{\circ} \times(T-298.15 K)\right)}{T^2} \partial T$$

again assuming that the lower temperature limit is the standard state T°. And when we do so, after some calculus and a significant amount of algebra, we end up with the same equation in the Kirchoff's Law discussion in Sec. 6.3.1.

6.4: Chemical reactions and chemical potential

In the preceding section we calculated $\Delta_r G^\circ$ of a reaction at the standard state (or $\Delta_r G$ at a non-standard temperature) assuming that the reaction went to completion. In a mathematical sense, what we were doing is integrating the partial change of Gibbs energy ∂G with the lower limit representing the initial reactant state and the upper limit defined as the product state as shown in Equation 6.9: `\int^{\sum_{products}{}}\upsilon \cdot {\Delta_fG}^{\diamond }_m}_{\sum_{reactants}{}}\upsilon {{\cdot \Delta }_fG}^{\diamond }_m}{}\partial \left(\Delta_rG\right)=\sum_{products}{}\upsilon \cdot {\Delta_fG}^{\di`

This is depicted graphically in Figure 6.4A, in which a negative $\Delta_r G^\circ$ implies that a reaction will go to completion. This is because a process that exudes Gibbs energy is also creating a net gain in total entropy which the 2^{nd} Law allows.

However, the ides that chemical reaction yields are either 0% or 100% clearly isn't correct. After all, if this is true then why are synthetic chemists working hard to optimize reaction conditions? The problem is that we didn't consider how $\Delta_r G$ changes as a function of the extent of reaction "ϵ", which is a unitless parameter that varies from ϵ = 0 (all reactants) to ϵ = 1 (all products). As shown in Figure 6.4B, if there is a minimum in the Gibbs energy below either product or reactant at point ϵ = α, then the reaction will stop there as the most total entropy is generated at that point. The reaction yield is thus determined by the value of α.

We can use chemical thermodynamics to determine the yield of a reaction. What we know is that $\Delta_r G = \frac{\partial G}{\partial \epsilon} = 0\ J$ when the reaction stops and the system has reached equilibrium. To go forward we need to know the mechanism by which $\Delta_r G$ changes as a spontaneous reaction proceeds forward after initiation. This will also allow us to calculate the reaction yield. As usual, we will start with a simple example.

6.4.1 Phase Changes. We will start analyzing chemical reactions using the example of ice melting. Although boring, it has the benefit of being very simple to analyze. First, we need to realize that a reaction yield is a percentage, and thus independent of how many moles of reactants initiate the reaction. This points towards the thermodynamic drive being an intensive variable. In fact, it's the energy per mole, which must change throughout a reaction as there must be an energetic consequence to chemicals being *removed from* or *added into* a system. Note that the addition of chemicals into a system represents the creation of products, while the reactants are removed.

In our previous derivations of U, H, A and G we never considered that the moles could change. As this is unavoidable in a chemical reaction, we have to revisit our equations for energy starting with internal energy U, the change of which is:

$$\partial U = -P\partial V + T\partial S + \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n\,(6.10)$$

Likewise:

$$\partial H = V\partial P + T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n\,(6.11)$$

$$\partial A = -P\partial V - S\partial T + \left(\frac{\partial A}{\partial n}\right)_{V,T} \partial n\,(6.12)$$

$$\partial G = V\partial P - S\partial T + \left(\frac{\partial G}{\partial n}\right)_{P,T} \partial n\,(6.13)$$

This is all rather unfortunate, because it appears that all four of our energy equations just became more complicated with the addition of new terms! However, this is in fact not quite the case. For example, we know that $H = U + PV$, for which the change in enthalpy is:

$$\partial H = \partial U + \partial (PV)$$

Substituting in Equation 6.11 for ∂H and Equation 6.10 for ∂U:

$$V\partial P + T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = -P\partial V + T\partial S + \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n + \partial (PV)$$

which can be simplified:

$$V\partial P + T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = -P\partial V + T\partial S + \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n + P\partial V + V\partial P$$

After doing some cancellation and taking like terms to one side: $V\partial P - V\partial P + T\partial S - T\partial S + \left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n$ which further simplifies to:

$$\left(\frac{\partial H}{\partial n}\right)_{P,S} \partial n = \left(\frac{\partial U}{\partial n}\right)_{V,S} \partial n$$

Division by ∂n leads to $\left(\frac{\partial H}{\partial n}\right)_{P,S} = \left(\frac{\partial U}{\partial n}\right)_{V,S}$. Similar derivations reveal that:

$$\left(\frac{\partial G}{\partial n}\right)_{P,T} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial H}{\partial n}\right)_{P,S} = \left(\frac{\partial U}{\partial n}\right)_{V,S} = \mu \tag{6.4.1}$$

Equation 6.4.1 demonstrates that, however we express the change in energy per mole and whatever conditions are held constant, we are dealing with the same thermodynamic quantity. We will call it the chemical potential μ, which can be used to calculate the change in energy with increasing / decreasing moles of a substance in a system as $\mu \cdot \partial n$. For the purposes of this chapter and later ones, we will assume conditions of constant temperature and pressure for all reactions.

6.4.1.1 Ice melting. We will study the melting of an ice cube into liquid water as characterized by the chemical potentials μ_{ice} and μ_{water}. Let us first assume that the ice and water are in equilibrium, which requires that change in Gibbs energy is 0 J if any of the ice melts (or water freezes). Mathematically this is expressed as:

$$\partial (\Delta_r G) = \mu_{water} \partial n_{water} + \mu_{ice} \partial n_{ice} = 0\ J$$

where we have added the change in Gibbs energy in each phase to represent the total. Since the ice and water are both H_2O, then it must be true that $\partial n_{ice} = -\partial n_{water}$, which we can insert into the above as: $\mu_{water} \partial n_{water} - \mu_{ice} \partial n_{water} = 0\ J$. Rearranging terms:

$$(\mu_{water} - \mu_{ice})\, \partial n_{water} = 0\ J$$

Here, we have to figure out whether $(\mu_{water} - \mu_{ice})$ or ∂n_{water} is 0. To resolve we can perform the following experiment- put an ice cube into water at 0 °C. If you wait long enough, the cube will transform into a sphere, which means that it is possible to have microscopic mass transfer even at equilibrium which implies $|\partial n_{water}|$ doesn't have to be 0, even at equilibrium. Therefore, it must be true that $\mu_{water} - \mu_{ice} = 0\ J/mol$, and thus $\mu_{water} = \mu_{ice}$ at equilibrium. We just proved that the chemical potentials of things at equilibrium are equal!

Let's now raise the temperature of the ice / water system so the ice melts. The system is no longer at equilibrium, and the irreversible melting of ice increases the total entropy of the Universe. Under conditions of constant temperature and pressure this requires a negative change in Gibbs energy: $\Delta_r G = \mu_{water} \Delta n_{water} + \mu_{ice} \Delta n_{ice} < 0\ J$

which trickles down to $(\mu_{water} - \mu_{ice})\, \Delta n_{water} < 0\ J$ for the same reasons as above. Now since $\Delta n_{water} > 0\ mol$ because the ice is melting, then it must be true that $\mu_{water} - \mu_{ice} < 0\ J/mol$, requiring $\mu_{water} < \mu_{ice}$. Consequently, when a reaction occurs, mass transfers from the high chemical potential to the lower chemical potential state. While this is true for ice melting, it's also true for any chemical reaction including the ones where actual chemical bonds are broken and formed.

6.4.2 Real Chemical Reactions: Changing chemical potential. Based on the discussion above it is clear that the net change of the chemical potential of a spontaneous reaction ($\Delta_r\mu$) is negative. Of course, all reactions eventually stop at which time the chemical potentials of reactants and products must be equal and $\Delta_r\mu = 0\ J/mol$. Thus, there must be some mechanism for the potentials of reactants and products to change though the course of the reaction. Let’s study a reaction in the gas phase, starting with 1 mole of a reactant at the standard state. The chemical potential will decrease as the reaction progresses, but the question is how do we measure this change in μ? Here is a simple observation- as the reactant is consumed, its partial pressure decreases. This is akin to performing work (see Sec. 2.2):

$$\Delta w = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$$

We insert the perfect gas relationship to modify the work equation for pressure:

$$\Delta w = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right) = -nRT \cdot \ln\left(\frac{\frac{nRT}{P_f}}{\frac{nRT}{P_i}}\right) = -nRT \cdot \ln\left(\frac{P_i}{P_f}\right) = nRT \cdot \ln\left(\frac{P_f}{P_i}\right)$$

We stipulated that the initial pressure P_i is the standard state pressure P° = 1 bar (recall that the $^\circ$ symbol refers to the standard state, which is 298.15 K and 1 bar pressure). Furthermore, the pressure is actually the reactant’s partial pressure, not total pressure, since the product(s) will also contribute to the total pressure. Next we divide by n to calculate the work energy per mole of reactant:

$$\frac{\Delta w}{n} = RT \cdot \ln\left(\frac{P_f}{P^\circ}\right)$$

This should be added to the initial energy per mole (μ°, the chemical potential at the standard state) to represent the change in the chemical potential of the reactant as it is depleted during the course of the reaction:

$$mu = \mu^\circ + RT \cdot \ln\left(\frac{P_f}{P^\circ}\right) \tag{6.4.2}$$

We can make another modification using Dalton’s Law, which states that the partial pressure of a gas can be expressed as the total pressure times the mole fraction of that gas. In other words, $P_f = \chi \cdot P$, and thus:

$$mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right) \tag{6.4.3}$$

where \chiup is the mole fraction of the gas which changes through the course of the reaction. Initially \chiup=1, and if the reactant is totally consumed then \chiup=0 in the final state.

Equation ??? allows us to connect the changing mole fraction’s effect on a reaction’s$partial\left(\Delta_r G\right)$ via the chemical potential. To this end recall: $\partial G = V\partial P - S\partial T + \left(\frac{\partial G}{\partial n}\right)_{P,T} \partial n$, which we simplify for constant pressure and temperature conditions ($\partial P = \partial T = 0$) and for the fact that multiple species (reactants and products) exist:

$$\partial G = \sum \left(\frac{\partial G}{\partial n}\right)_i \cdot \partial n_i = \sum \mu_i \cdot \partial n_i$$

where we used $\left(\frac{\partial G}{\partial n}\right)_i = \mu_i$ and inserted an index “i” to delineate the various chemical participants (the reactants and products). We will analyze the energies further using the extent of the reaction “ϵ” that was introduced earlier. Recall that ϵ varies from 0 → 1, where $\epsilon = 0$ represents the initial reactant state and $\epsilon = 1$ is for an all product state. A graph of G vs. ϵ is shown in Fig. 6.5A, where we can see that $\frac{\partial G}{\partial \epsilon}$ is the quantity of interest. Initially, $\frac{\partial G}{\partial \epsilon}$ is negative near $\epsilon = 0$. Does this make the reaction spontaneous? To answer, we assume that $\partial\epsilon$ is positive (the reaction goes forward) and as a result ∂G must be negative which is the definition of a spontaneous reaction. At some point $\frac{\partial G}{\partial \epsilon} = 0\ J$ and the reaction stops. It is here that the most negative reaction $\Delta_r G$ is realized as determined using:

$$\Delta_r G = \int_0^\alpha \frac{\partial G}{\partial \epsilon}\partial\epsilon$$

which is also where the most total entropy is generated. We see this more clearly in Figure 6.5B, which is a plot of the derivative $\frac{\partial G}{\partial \epsilon}$ vs. ϵ. The negative area (shaded red) starting from the reactant side to point $\epsilon = \alpha$ generates the most negative net $\Delta_r G$ possible. Further progression of the reaction past point α diminishes the net $\Delta_r G$ as the additional Gibbs energy contribution is positive (blue shaded area), which consumes the net entropy and is thus not allowed.

The extent of the reaction ϵ is related to the changes in the moles of products and reactants by the simple relationship: $\partial n = \upsilon \cdot \partial\epsilon$, where υ represents the stoichiometric coefficient of a reactant or product. As such, υ is positive for products, because these “appear” during the reaction, whereas υ is negative for reactants since they “disappear”. We insert these ideas into the change of Gibbs energy:

$$\partial G = \sum \mu_i \cdot \partial n = \sum_{products} \upsilon_i \cdot \mu_i \cdot \partial\epsilon - \sum_{reactants} \upsilon_i \cdot \mu_i \cdot \partial\epsilon = \left(\sum_{products} \upsilon_i \cdot \mu_i - \sum_{reactants} \upsilon_i \cdot \mu_i\right) \cdot \partial\epsilon$$

Division of $\partial\epsilon$ on both sides reveals:

$$\frac{\partial G}{\partial \epsilon} = \sum_{products} \upsilon_i \cdot \mu_i - \sum_{reactants} \upsilon_i \cdot \mu_i$$

Using this relationship with the mole fraction (\chiup)-dependent chemical potentials $\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{\chi \cdot P_i}{P^\circ}\right)$ allow us to find the composition of a reactive system when the reaction reaches equilibrium as defined by $\frac{\partial G}{\partial \epsilon} = 0\ J$. In other words, we can determine the reaction yield.

For any of this to practically work, we must insert real data into the thermochemical relationship above. The chemical potential of a reacting entity is its per molar Gibbs energy due to the fact that: $\mu = \frac{\partial G}{\partial n} = \frac{G}{n} = G_m$, which is true because energy and moles are extensive quantities and can be integrated as:

$$\mu = \frac{\int_{0\ J}^{G} \partial G}{\int_{0\ mol}^{n} \partial n} = \frac{G}{n} = G_m$$

Due to the relative nature of energy, we use the standard state per molar Gibbs energy of formation from a data table to represent the chemical potential, i.e. $\mu^\circ = G_m^\circ = \Delta_f G_m^\circ$. When we put this all together, we see that $\mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$ is equivalent to $\Delta_f G_m = \Delta_f G_m^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$. This also means that $\frac{\partial G}{\partial \epsilon}$ is the “instantaneous” $\Delta_r G$ at point ϵ along the reaction.

At this point you may be overwhelmed with the complexity of composition-dependent chemical potentials derived above. We will stop and work some examples that will hopefully make all of this much more clear. First, we will determine the reaction yield for something simple:

A(g) → B(g)

Each species has its own chemical potential and mole fraction. Starting with $\Delta_r G$:

$$\Delta_r G = \nu_B \cdot \mu_B - \nu_B \cdot \mu_A$$

$$= \nu_B \cdot \mu_B^\circ + \nu_B \cdot RT \cdot \ln\left(\frac{\chi_B \cdot P}{P^\circ}\right) - \nu_A \cdot \mu_A^\circ - \nu_A \cdot RT \cdot \ln\left(\frac{\chi_A \cdot P}{P^\circ}\right)$$

$$= \left(\nu_B \cdot \mu_B^\circ - \nu_A \cdot \mu_A^\circ\right) + RT \cdot \left(\nu_B \cdot \ln\left(\frac{\chi_B \cdot P}{P^\circ}\right) - \nu_A \cdot \ln\left(\frac{\chi_A \cdot P}{P^\circ}\right)\right)$$

Applying the identities: $y \cdot \ln(x) = \ln(x^y)$; $\ln(x) - \ln(y) = \ln\left(x \cdot y^{-1}\right)$; and $x^A \cdot x^{-B} = x^{A-B}$:

\[\Delta_rG=\left({\nu }_B\cdot {\mu }^

ParseError: invalid DekiScript (click for details)

ParseError: "}" expected (click for details)

\right){\left(\frac{P}{P{}^\circ }\right)}^{{\nu }_B-{\nu }_A}\right] \nonumber \]

The stoichiometric coefficients ($\nu_{A,B}$) are equal to 1 mol due to the 1:1 stoichiometry of A and B in this example. This allows us to remove the pressure term: $\left(\frac{P}{P^\circ}\right)^{\nu_B - \nu_A} = \left(\frac{P}{P^\circ}\right)^0 = 1$. We can also insert the definition of the initial chemical potentials as the formation Gibbs energy: $\mu^\circ = \Delta_f G_m^\circ$; thus, we can simplify $\Delta_r G$ as:

$$\Delta_r G = \Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ + RT \cdot \ln\left(\frac{\chi_B}{\chi_A}\right)$$

What is the above relationship good for? We assume that most chemical reactions will occur, but we just don't know how far, so we use the above relationship to determine χ_B and χ_A at equilibrium, which will give us the reaction yield. And at the end of a reaction $\Delta_r G = \nu_B \cdot \mu_B - \nu_B \cdot \mu_A = 0\ J$, which means that:

$$0\ J = \Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ + RT \cdot \ln\left(\frac{\chi_B}{\chi_A}\right)$$

allowing us to simplify the above to:

$$\Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ = -RT \cdot \ln\left(\frac{\chi_B}{\chi_A}\right) \tag{6.4.4}$$

Note that $\Delta_f G_{B,m}^\circ - \Delta_f G_{A,m}^\circ = \Delta_r G^\circ$ is what you calculate from a standard Hess's Law question. This quantity is *not* the same as $\Delta_r G$, which accounts for the changing chemical potential as the reaction occurs due to the $RT \cdot \ln\left(\frac{\chi_B}{\chi_A}\right)$ term.

With equation 6.17 we can calculate χ_B and χ_A at equilibrium to determine the reaction yield. First, we must account for the fact that the mole fractions are not independent of each other because $\chi_A + \chi_B = 1$. Let's make a table that details the stoichiometries of the product and reactants before and after the reaction, as well as the resulting mole fractions. We initially begin with "n" moles of A. At the end of the reaction a certain fraction of A has reacted, which we will call α. As a result, there are n-n•α moles of A and n•α moles of B at the end:

	A	**B**
Initial	n	0
Equilibrium	n − n·α	n ·α
Mole fraction	1- α	α

Here you can see that, if α=0, then no reaction has taken place. If α=1 then all the A reacted to become B giving a 100% yield. The mole fractions of products and reactants at equilibrium are determined by adding up the total number of moles at equilibrium: $n_A + n_B = n - n \cdot \alpha + n \cdot \alpha = n$. Thus, the mole fraction of A at equilibrium is $\chi_A = \frac{n - n \cdot \alpha}{n} = 1 - \alpha$ and $\chi_B = \frac{n \cdot \alpha}{n} = \alpha$. Plug these into the preceding relationship for the chemical potential and mole fractions, Equation 6.17:

$$\Delta_r G^\circ = -RT \cdot \ln\left(\frac{\alpha}{1 - \alpha}\right)$$

With a numerical value for $\Delta_r G^\circ$ from a Hess's Law calculation, we can thus determine α which is the reaction yield. To demonstrate, we will apply some limiting scenarios; let's say that the difference in Gibbs formation energies of A and B is 0 J. In this case, we are solving:

$$0\ J = -RT \cdot \ln\left(\frac{\alpha}{1 - \alpha}\right)$$

which simplifies to: $\ln\left(\frac{\alpha}{1-\alpha}\right) = 0$. Taking the exponential of both sides: $exp\left(\ln\left(\frac{\alpha}{1-\alpha}\right)\right) = exp\,(0)$. The result is: $\frac{\alpha}{1-\alpha} = 1$, and thus α=0.5. The result is sensible- if there is no driving force to form either products or reactants, then the reaction goes to ½ completion! This is graphically illustrated in Figure 6.6, along with scenarios of $\Delta_r G^\circ = 2\ J$, $\Delta_r G^\circ = -2\ J$, and finally $\Delta_r G^\circ = -10\ J$. The way that the $G\ vs.\ epsilon$ curve bends downwards is due to the entropy of mixing between the product and reactant as discussed below.

6.4.3 Entropic Contribution. Here we will examine why a reaction with a $\Delta_r G^\circ = 0\ J$, technically non-spontaneous, has a product yield of 50%. While we could simply say "because the math worked out that way" as shown in the previous section, there is a more fundamental reason. It is due to that fact that changes in Gibbs energy is derived from enthalpy and entropy, and it is entropy that can drive a reaction forward even when it is not spontaneous. To understand, recall that the change in a system entropy per mole is: $\Delta S_m = -R \cdot \ln\left(\frac{P_f}{P_i}\right)$ at constant temperature, which when multiplied by -T gives us:

$$-T \cdot \Delta S_m = RT \cdot \ln\left(\frac{P_f}{P_i}\right) = RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$$

where $P_f = \chi \cdot P$ from Dalton's Law and $P_i = P^\circ$ due to standard state conditions. This is the same composition-adjustment factor that was applied to the chemical potential, Equation 6.16: $\mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right)$. The way to understand the result is the fact that it is entropically favorable

for chemical "A" to mix with "B", but the only way to do so is for some of "A" to react to become "B"! This is why most of the $G\ vs.\ epsilon$ curves in Figure 6.5 bow downwards near the middle of the graph, where mixing is greatest. We see that more products form in the case of

”””

$\Delta_r G^\circ =$ -10 kJ due to the generation of greater total entropy near the ~100% reaction yield point. In this situation, the reaction likely produces a lot of heat (i.e. has a large negative enthalpy), which adds significant exterior entropy. Hence, it is this extra generation of exterior entropy due to a near-completion of the reaction that overwhelms the entropic effects of mixing in the system that wants to stop at the ½ way point.

6.5: Equilibrium Constants

Let’s derive a general expression for the thermochemistry of chemical reactions with arbitrary numbers of reactants and products; example problems 6.3 and 6.4 are also helpful for your understanding in this regard. For any reaction:

\[\Delta_rG=\sum_{products}{}{\upsilon }_i\cdot {\mu }_i-\sum_{reactants}{}{\upsilon }_i\cdot {\mu }_i=\left(\sum_{products}{}{\upsilon }_i\cdot {\mu }^

ParseError: invalid DekiScript (click for details)

{\prod_{reactants}{}{\left(\frac

ParseError: invalid DekiScript (click for details)

\right] \nonumber \]

The argument of the natural log (highlighted in red) has a name. At the beginning of a reaction it is called the reaction quotient and is symbolized with the letter “Q”. If this ratio is determined at equilibrium, it is called the equilibrium constant “K”. Consequently, at equilibrium:

$$K=exp\left(\frac{-\left\{\sum_{products}\upsilon_i\cdot\mu_i-\sum_{reactants}\upsilon_i\cdot\mu_i\right\}}{RT}\right)=exp\left(\frac{-\Delta_rG^\circ}{RT}\right) \tag{6.5.1}$$

Equation 6.5.1 reveals that a simple Hess’s Law calculation can be used to determine Δ_rG°, which, in turn defines the equilibrium concentrations and reaction yield. It is important to note that this relationship was defined for a gas phase reaction and may not be rigorously true for a chemical process occurring in solution. These topics are discussed in Chapter .7

6.5.1 Temperature dependent equilibrium constants

There is a subtlety to Equation 6.18, which is that the equilibrium constant K is a function of Δ_rG° and T, although Δ_rG° is strictly defined from the data in Table 6.1 for T=298.15 K. Consequently, it isn’t straightforward to determine how the equilibrium constant changes with temperature. To do so, we first note:

$$\Delta_rG^\circ=-RT\cdot\ln(K) \tag{6.5.2}$$

where T must be the standard state temperature. Our approach to determine the how K changes with temperature, and then add that change onto the standard state K, as determined where T = 25 °C. First, we rearrange Equation 6.19: $\ln(K)=\frac{-\Delta_rG^\circ}{RT}$ and take the temperature derivative:

$$\frac{\partial\ln(K)}{\partial T}=\frac{1}{R}\frac{\partial\frac{-\Delta_rG^\circ}{T}}{\partial T}=\frac{\Delta_rH^\circ}{RT^2}$$

using the Gibbs-Helmholtz equation. Next the partials are rearranged as: $\partial\ln(K)=\frac{\Delta_rH^\circ}{RT^2}\partial T$. This allows us to determine how K changes over a finite temperature range:

$$\int_{\ln[K(T_1)]}^{\ln[K(T_2)]}\partial\ln(K)=\int_{T_1}^{T_2}\frac{\Delta_rH^\circ}{RT^2}\partial T$$

Assuming $T_1=T^\circ$ (the standard temperature), and following the established rules of integration:

$$\ln[K(T_2)]=\ln[K(T^\circ)]+\frac{\Delta_rH^\circ}{R}\left(\frac{T_2-T^\circ}{T_2\cdot T^\circ}\right) \tag{6.5.3}$$

Note that in the derivation of Equation 6.20 that the integration of the enthalpy did not include temperature dependence (the value of Δ_rH° from a data table is valid only at T = 25 °C). We previously demonstrated how to account for enthalpy’s temperature dependence in Chapter 3 using the heat capacity; regardless, inclusion of this factor makes the final result very complex so we will stick with this approximation here.

Conclusion

In this chapter we revealed that the absolute value of energy, whether internal, enthalpic or Gibbs' energy, of a real chemical substance is unfortunately unknowable. This forces us to tabulate thermodynamic data relative to a standard state defined by the intensive variables pressure and temperature. We can use these data to predict reaction yields with good accuracy at the standard state. It is possible to obtain such information outside the standard state, say at a higher temperature, at the expense of performing somewhat more complex calculations. From here on we will now move away from gases and study chemical processes in condensed phases (liquid and solid). However, you will find our knowledge of thermodynamic processes becomes increasingly more abstract and inexact as a result.

CHAPTER OVERVIEW

7: Solutions and Colligative Properties

Thus far we have studied energy from work and heat and used that knowledge to understand chemical reactions. We can even calculate a reaction yield without actually going into the lab to measure it! However, all of these have been applied solely to the gas phase, which is attractive because we don’t have to worry about the energetics of intramolecular interactions (ideal gases don’t interact). Here we move on, as many important chemical phenomena occur in liquids and solids such as the synthesis of DNA in your living cells and the geological creation of oil from ancient carbon. How do the thermodynamic principles we have studied thus far change for liquids and solids? To answer, we will start with the liquid phase analogy of a gas expanding, which is the mixing of salt in water.

7.1: Partial Vapor Pressure

You have to do very little to understand the thermodynamics of a pure liquid like a cup of water, or a solid substance such as a teaspoon of salt. There are data tables with all the relevant information ($\Delta_f H_m^\circ$, $\Delta_f G_m^\circ$, S_m°, etc., see Table 6.1); you can simply look them up. You can also sit down and watch the cup of water, but probably there isn't much to see (and the teaspoon of salt is doing even less!). It's all, rather… boring.

Let's do something much more fun! Take the teaspoon of salt and add it to the water, and start answering some questions- does it dissolve? Does the water get warm, cold, or stay the same? Does the energy of the water and salt change? Now we are getting somewhere, and to begin we probably need a way to determine how the energies of things change when they are mixed. As you can imagine, this could be extremely complicated. Initially the water molecules interacted with each other via hydrogen bonds, and this is still true after adding salt except for the fact that the water is also interacting with the salt. Also salt tends to dissociate into ions (Na^+ and Cl^- for example); surely there are energetic and entropic consequences for that although we also have to consider that not all the salt may dissolve. Overall, this seems like a very complicated system to analyze due to the enthalpy of water interacting with the dissolved ions and the increase in entropy due to the salt dissociating. In fact, all of this is so complex that we are going to avoid directly analyzing the liquid solution altogether.

Fortunately, there is a much easier way to study the thermodynamics of condensed phases and processes such as mixing. To this end we examine the vapors that are in equilibrium with the liquid. Recall in Ch. 6 that we determined that the intensive variables of substances in equilibrium are all equal. These include temperature, pressure, as well as the chemical potentials which are the most important. Concerning the mixing of salt and water, we know that the chemical potential of water drops due to the addition of salt. Since the water vapor and liquid water are assumed to always be in equilibrium, the vapor experiences *the exact same change in chemical potential!* Consequently, measuring the very complex interactions due to mixing in the liquid phase is equivalent to measuring the thermodynamic changes in the vapor (i.e. gas) phase, which is great because we have learned in previous chapters exactly how to do that!

As it applies to mixing, we have to determine what properties of the vapor change when the liquid (i.e. the equilibrium partner) mixes with something like salt, and how those changes perturb the vapor's chemical potential. Using liquid water at room temperature and pressure as an example, we know that having a cup of water in a very dry room will result in evaporation. This continues until the partial water vapor pressure reaches 3,200 Pa ($\sim$0.03 atm), as this is the equilibrium vapor pressure under standard conditions. If salt is added to the bath, some of the water vapor will return to the liquid to "dilute" the salt that sullied the pure water; you might recognize this as Le Chatelier's principle that describes how a system resists change. Thus, the partial pressure of water vapor will decrease. It is this decrease in the vapor's partial pressure that allows us to calculate $\Delta_{mix}\mu$ for the liquid.

There is another way to view this dynamic as shown in Figure 7.1. While water will vaporize off the surface of a cup of the pure liquid as shown in the left, it will do so to a lesser extent if salt is present as shown on the right. Here, we can think of the salt as forming a barrier at the surface of the liquid, which hinders water from vaporizing off of it. Perhaps the ions "hold down" the water molecules, which prevents them from flying off into the vapor state? Regardless, the vapor pressure from a saturated aqueous NaCl solution has been measured to be $\sim$2,700 Pa, which is about a 15% less than the vapor pressure of pure liquid water.

Chemical potential is the per molar Gibbs energy, and we need to know how the Gibb's energy of a vapor changes due to a drop in its partial pressure at a constant temperature. This is very easy as we determined in Chapter 5 that the ΔG of a gas is equal to reversible work: $\Delta G = -nRT \cdot \ln\left(\frac{V_2}{V_1}\right)$, with initial volume V_1 and final volume V_2. As we are concerned with pressure rather than volume, we insert the perfect gas law to show:

$$\Delta G = -nRT \cdot \ln\left(\frac{V_2}{V_1}\right) = -nRT \cdot \ln\left(\frac{\frac{nRT}{P_2}}{\frac{nRT}{P_1}}\right) = nRT \cdot \ln\left(\frac{P_2}{P_1}\right)$$

where P_2 is the vapor pressure of the salted water and P_1 is from pure water. When we divide by the number of moles n we now have an equation for the change in chemical potential: $\frac{\Delta G}{n} = \Delta\mu = RT \cdot \ln\left(\frac{P_2}{P_1}\right)$

Some notational changes are needed because we are discussing mixtures. Specifically, we state $P_2 = P_i$, where P_i is the partial pressure of substance " i " in the mixed state (we must keep track of what is what using the " i " subscript because there must be two or more chemical substances when making a solution). If we assume that the initial pressure is derived from the pure liquid, then we call it P_i^* which is the pure partial pressure of liquid " i ". Inserting these notational differences:

$$\mu_i = \mu_i^\circ + \Delta\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{P_i}{P_i^*}\right) \tag{7.1.1}$$

The equation above represents a way to determine the change in a vapor's chemical potential via an alteration of its partial pressure. A drop in the partial pressure would likely result from dilution of the source liquid by addition of salt, or anything else for that matter. And the $\Delta\mu_i$ of the vapor is exactly the same as the $\Delta\mu_i$ of the liquid, assuming that the vapor and liquid are in equilibrium.

7.2: Partial Pressure Measurements and Raoult’s Law

It is fantastic that we have a simple way to quantify the changes in the thermodynamic variables of liquids by hijacking measurements of the equilibrated vapor phase’s μ, as determined by the change in the vapor’s partial pressure. And thus we can mix any two miscible substances, salt and water or perhaps something more risqué like gin and juice (ethanol and water) and measure the changes in the individual substances’ vapor pressures to determine $\Delta \mathrm{G}_m$, $\Delta \mathrm{H}_m$, and $\Delta \mathrm{S}_m$ for mixing. However, the measurement of partial pressure of a vapor is rather complex even by today’s standards. Perhaps there is an easier way to relate the partial pressure of a vapor to the concentration of the liquid in solution? For example, if we have a cup of pure water then the partial pressure of the $\mathrm{H_2O}$ vapor is 3,200 Pa. Upon dilution with an extremely large quantity of ethanol the water partial pressure must drop to almost nothing, $\sim$0 Pa. Thus, the water vapor’s partial pressure decreases from 3,200 Pa $\rightarrow$ 0 Pa as $\backslash\mathrm{chiup}_{H2O}$ decreases from 1 $\rightarrow$ 0, where $\backslash\mathrm{chiup}_{H2O}$ is water’s mole fraction in the liquid solution.

François-Marie Raoult, an electrochemist, discovered that a vapor’s partial pressure may be linear function of the liquid’s molar concentration, especially if the liquid is very dilute. Mathematically this is expressed as:

$$P_i = P_i^* \cdot \frac{n_i}{n_{total}} = P_i^* \cdot \chi_i \tag{7.2.1}$$

Equation 7.2.1 is Raoult’s Law, and note how it yields the pure partial pressure if the i^{th} species is pure (χ_i = 1) and 0 Pa if the i^{th} species is infinitely diluted (χ_i = 0). Shown in Figure 7.2 A is a graph of the partial pressures of benzene + toluene solution as a function of their mole fractions, including lines derived from equation 7.2. The use of Raoult’s Law is ideal as it provides a near-perfect fit over the entire concentration range! However, shown in Figure 7.2 B are data for a water + ethanol solution, which demonstrates that Raoult’s Law doesn’t always work well. These situations are less than ideal and will be discussed further in later sections of this chapter.

7.3: Excess Functions and Ideal Solutions

Raoult's Law gives us a starting point to analyze the thermodynamics of mixtures in much the same way that the perfect gas law did in Chapter 1. We will use it to define several new thermodynamic variables for liquid mixtures; these are called "excess functions" and we will begin with the excess volume $\mathit{\Delta}_{mix}V$. To describe it we have to define a few terms; first, the volume per mole of liquid "A" in its pure form is $V_{m,A}$. This is defined such that if we have a glass full of liquid "A" and add one more mole of "A" to it, then the volume will increase by $V_{m,A}$. When expressed mathematically this is $V_{m,A}=\left(\frac{\partial V}{\partial n_A}\right)_{P,T}$, which is called a pure partial molar volume. You are actually quite familiar with this concept; if you add a mole (18 g) of water to water, the volume increases by $\sim$18 mL because the density of water is exactly 1.0 g/mL. Thus, $V_{m,H2O}=18\ mL/mol$. However, if we were to add 1 mole of water to a large quantity of ethanol, then the total solution volume would only increase by $\sim$14 mL! It is this difference that represents the excess volume of mixing.

To generalize, we state that if a glass contains liquid "B", the volume increase that occurs after the addition of a mole of "A" is:

$$\underline{V}_A=\left(\frac{\partial V}{\partial n_A}\right)_{P,T,n_B\neq n_A}$$

where the subscript "$n_B\neq n_A$" means that we are studying a solution that has more than one component. In the water + ethanol example $\underline{V}_{H2O}=14\ mL/mo\ln eq V_{m,H2O}$. In this situation there is a non-zero excess mixing volume ($\mathit{\Delta}_{mix}V$), which is defined as:

`{\mathit{\Delta}}_{mix}V=n_A\left({\underline{V}}_A-V_{m,A}\right)+n_B\left({\underline{V}}_B-V_{m,B}\right) \\label{7_3_}`

where n_A and n_B are the total number of moles of "A" and "B" in the resulting solution. Of course we had to add in the volume for component "B" into Equation 7.3 for $\mathit{\Delta}_{mix}V$, after all we can't make a solution just out of liquid "A"! In the case of a water + ethanol solution the excess volumes $\underline{V}_{H2O}$ and $\underline{V}_{EtOH}$ are shown in Figure 7.3, where it can be seen that they are continuously changing functions of the composition of the liquid.

It is important to understand that the excess solution volume, Equation 7.3, is not the same as the total solution volume. For example, adding water to water makes $\mathit{\Delta}_{mix}V$ = 0 mL/mol. To find $\mathit{\Delta}_{mix}V$ for the addition of water to a very large quantity of ethanol we look at Figure 7.3 to find $\underline{V}_{H_2O}$= 14.1 mL/mol, while the partial molar volume of ethanol is the same as the pure partial volume, $\underline{V}_{EtOH}=V_{m,EtOH}=$ 58.7 mL/mol. Thus the excess mixing volume upon addition of 1 mol water to a large excess of ethanol is: $\mathit{\Delta}_{mix}V=1\ mol\cdot(14.1-18.0)\ mL/mol+0\ mL=\ -3.9\ mL$. To check your understanding, perform the same calculation on the addition of ethanol to a large volume of water, where the partial molar volume of ethanol is $\underline{V}_{EtOH}$ = 54.9 mL/mol (you should find $\mathit{\Delta}_{mix}V=\ -3.8\ mL)$. One last item of interest is the fact that the partial molar volume data shown in Figure 3.7 are nearly mirror images of each other. This is no accident and is explained by a Gibbs-Duhem equation discussed in the extra information section.

There are excess functions for all thermodynamic variables, which are listed below:

$$\mathit{\Delta}_{mix}U=\sum_{i=1}^{\alpha}n_i\left(\underline{U}_i-U_{m,i}\right)\tag{7.3.1}$$

$$\mathit{\Delta}_{mix}H=\mathit{\Delta}_{mix}U+P\cdot\mathit{\Delta}_{mix}V=\sum_{i=1}^{\alpha}n_i\left(\underline{H}_i-H_{m,i}\right)\tag{7.3.2}$$

$$\mathit{\Delta}_{mix}S=\sum_{i=1}^{\alpha}n_i\left(\underline{S}_i-S_{m,i}\right)\tag{7.3.3}$$

$$\mathit{\Delta}_{mix}G=\mathit{\Delta}_{mix}H-T\cdot\mathit{\Delta}_{mix}S=\sum_{i=1}^{\alpha}n_i\left(\underline{G}_i-G_{m,i}\right)\tag{7.3.4}$$

In these equations α number of components in the solution; generally we will use α = 2 (for example, water and ethanol) for simplicity.

With the excess functions are defined we can examine what makes a solution "ideal". Specifically, the components "A" and "B" of an ideal solution obey Raoult's Law and have the following properties:

1. The partial volumes of the components in solution are identical to their pure partial volumes.
2. The components of an ideal solution interact the same way with their mixing partner as they do with each other.

The first property states that $\mathit{\Delta}_{mix} V = 0\ m^3$ for all ideal solutions. The consequence of the second property is that the internal energy of molecule "A", when in its pure form, is the same as when mixed with molecule "B". This means that $\mathit{\Delta}_{mix} U = 0\ J$. Combining these properties allows us to determine the enthalpy of mixing (Equation 7.5):

$$\mathit{\Delta}_{mix} H = \mathit{\Delta}_{mix} U + \mathit{\Delta}_{mix} (PV) = \mathit{\Delta}_{mix} U + V \cdot \mathit{\Delta}_{mix} P + P \cdot \mathit{\Delta}_{mix} V = \mathit{\Delta}_{mix} U + P \cdot \mathit{\Delta}_{mix} V$$

The $V \cdot \mathit{\Delta}_{mix} P$ is removed because we assume the pressure is constant; furthermore, $\mathit{\Delta}_{mix} U = 0\ J$ and $\mathit{\Delta}_{mix} V = 0\ m^3$ due to the fact that we are describing an ideal solution. As a result $\mathit{\Delta}_{mix} H = 0\ J$, which demonstrates that an ideal solution neither warms nor cools when "A" and "B" are mixed. As an example, let's recall that toluene and benzene obey Raoult's Law as seen in Figure 7.2A. Our chemical intuition tells us that these two aromatic molecules likely interact with each other and among themselves via \piup $-$\piup interactions; furthermore, they have similar volumes. As a result we can conclude that toluene and benzene form an ideal solution.

Let's study why ideal solutions mix, which must mean that $\mathit{\Delta}_{mix} G$ is negative. According to Equation 7.7:

$$\mathit{\Delta}_{mix} G = \mathit{\Delta}_{mix} H - T \cdot \mathit{\Delta}_{mix} S$$

and since $\mathit{\Delta}_{mix} H$ = 0 J, then $\mathit{\Delta}_{mix} G = -T \cdot \mathit{\Delta}_{mix} S$. Consequently entropy is entirely responsible for ideal solution mixing. For $\mathit{\Delta}_{mix} G$ to be negative then $\mathit{\Delta}_{mix} S$ must be positive which we will prove in the following derivation. In Sec. 7.1 we determined that the Gibb's energy change for component "A" in a mixture is: $\Delta G_A = n_A RT \cdot \ln\left(\frac{P_2}{P_1}\right)$, where the initial pressure is the pure partial pressure $(P_1 = P_A^*)$ and the final pressure is the partial pressure in the mixed state $(P_2 = P_A)$. As a result $\Delta G_A = n_A RT \cdot \ln\left(\frac{P_A}{P_A^*}\right)$, which can be further simplified by insertion of Raoult's Law: $P_A = P_A^* \cdot \chi_A$:

$$\Delta G_A = n_A RT \cdot \ln\left(\frac{P_A^* \cdot \chi_A}{P_A^*}\right) = n_A RT \cdot \ln(\chi_A)$$

Since there must be at least two species to form a mixture, we must add in the change in chemical potential of species "B" to calculate the total change:

$$\mathit{\Delta}_{mix} G = \Delta G_A + \Delta G_A = n_A RT \cdot \ln(\chi_A) + n_B RT \cdot \ln(\chi_B) \tag{7.3.5}$$

As the chemical potential is Gibbs energy per mole, we divide Equation 7.8 by total number of moles $n = n_A + n_B$:

\[\frac

ParseError: invalid DekiScript (click for details)

_{mix}G_m={\mathit{\Delta}}_{mix}\mu =\Delta {\mu }_A+\Delta {\mu }_B \nonumber \]

$$\begin{aligned} &= \frac{n_A}{n} RT \cdot \ln(\chi_A) + \frac{n_B}{n} RT \cdot \ln(\chi_B) \\ &= RT \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \end{aligned} \tag{7.3.6}$$

Given the $\mathit{\Delta}_{mix} G_m = -T \cdot \mathit{\Delta}_{mix} S_m$ relationship derived earlier, we can see that: $\mathit{\Delta}_{mix} S_m = -R \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$

which is always a positive quantity, and reveals that ideal solutions always mix due to the increase in entropy. The size extensive forms of the change in entropy is simply the per molar form multiplied by the total number of moles:

$$\mathit{\Delta}_{mix} S = -nR \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)) \tag{7.3.7}$$

7.4: Henry’s Law, Activity, and Ideal-Dilute Solutions

We learned from the previous section that the mixing of ideal solutions is an entropically driven process. However, not every combination of two liquids can be ideal as we know that many liquids don’t mix at all! Take for example water and ethanol, the data for which in Figure 7.2 B reveal that they do not follow Raoult’s Law. Mixing the two results in a temperature increase, and there is always a negative excess mixing volume; all of these data confirm the non-ideality of the water and ethanol interactions. Our intuition should be good enough to suspect that this is due to the disruption of water’s hydrogen bonding by ethanol.

In this section we will study the limits of the ideal approximations as expressed by Raoult’s Law, and what properties of liquid mixtures result in non-ideality. We will also study how to incorporate non-ideality into our thermodynamic analyses beginning with Henry’s Law. In 1803, William Henry published a paper on the dissolution of gases in water, most notably CO_2 as well as “oxygeneous” and “azoitc” gases. Henry’s Law can be used to determine the partial pressure of a vapor of a solution’s solute, where the solute is defined as a highly diluted component of a liquid mixture ($\chi_{solute} \rightarrow 0\ M$). Mathematically Henry’s Law is:

$$P_i = K \cdot \chi_i \tag{7.4.1}$$

where K is the Henry’s Law constant of substance $``i''$. Figure 7.4 reveals more clearly how this works, as it can be seen that Henry’s Law constant acts as a replacement for the pure partial pressure in Raoult’s Law. Hence, it is simply an empirical “fix” for Raoult’s equation when it doesn’t work for a diluted component in a solution. In a mixture where the solvent follows Raoult’s Law and the solute Henry’s, we refer to such as an ideal-dilute solution.

”””””””

7.4.1 Activity

Thus far we have shown how the chemical potential of component “i” of a solution, which is exactly $\mu_i = \mu_i^\circ + RT \cdot \ln\left(\frac{P_i}{P_i^*}\right)$, can be approximated using Raoult’s Law: $\mu_i = \mu_i^\circ + RT \cdot \ln(\chi_i)$ for an ideal solution or Henry’s Law: $\mu_i^\circ + RT \cdot \ln\left(\frac{K \cdot \chi_i}{P_i^*}\right)$ for the solute of an ideal-dilute solution. However, as we see in Figure 7.4 neither Henry’s nor Raoult’s laws are especially accurate for a non-ideal solution near the center of the graph. As a result, there is an ultimate empirical “fix” to calculate the chemical potential whereby the ratio of the measured partial pressure to the pure partial pressure of a component $\left(\frac{P_i}{P_i^*}\right)$ is simply called the activity “ a_i” of that component. The value of the unitless activity is exactly equal to $\left(\frac{P_i}{P_i^*}\right)$, which means that its inclusion into the equation for chemical potential:

$$\mu_i = \mu_i^\circ + RT \cdot \ln(a_i)$$

makes the expression work perfectly. The activity of a component changes as a function of solution composition, which makes the use of activity somewhat silly because it is simply another way to express the ratio $\left(\frac{P_i}{P_i^*}\right)$ that has to be measured for every solution concentration. To preserve a relationship to the mole fraction in a liquid mixture, activity can be expressed as:

$$a_i = \left(\frac{P_i}{P_i^*}\right) = \gamma_i \chi_i \tag{7.4.2}$$

where γ_i is a correction factor that forces the liquid mole fraction \({\chi }_i)to return the correct activity. As a result, the mixing excess Gibbs energy for a binary mixture of “A” and “B” is:

$$\Delta_{mix} G = nRT \cdot (\chi_A \cdot \ln(\gamma_A \cdot \chi_A) + \chi_B \cdot \ln(\gamma_B \cdot \chi_B))$$

$$\Delta_{mix} G = nRT \cdot (\ \chi_A \cdot \ln(\gamma_A) + \chi_B \cdot \ln(\gamma_B) + \chi\ _A \cdot \ln(\chi_A) + \chi_B \cdot \ln(\chi_B)) \tag{7.4.3}$$

Calculating activities requires measuring all the partial pressures of all the components of a solution, which is what we were trying to avoid using the concepts of ideal and ideal-dilute solutions. However, this approach may be necessary because Henry’s and Raoult’s Laws are really just approximations.

7.4.1.1 Excess Enthalpy and Activity

Activity can be used to understand what makes a solution non-ideal, which we already have shown means that $\Delta_{mix} H$ *is not* equal to 0. In other words, a solution becomes warm or cold after mixing the components. To this end we will create a phenomenological model for a non-zero Δ_{mix} H and use that to understand activity and thus the deviations from Raoult's Law. First, we take into account that, for a solution composed of "A" and "B", the enthalpy must be proportional to the total mass of solution n. Also, if the total mass is composed of only "A" or "B", then there is no mixing and thus no excess enthalpy. Furthermore, our model must have units of energy. An equation such as: $\Delta_{mix} H \ = nRT \cdot \chi_A \chi_B$

combines these effects. However, we must allow both the sign and magnitude of the excess enthalpy to change. As a result, we multiply this phenomenological relationship by "β", a fix-it factor, to yield:

$$\Delta_{mix} H = \beta \cdot nRT \cdot \chi_A \chi_B \tag{7.4.4}$$

If we insert the above into the expression for the change in Gibb's energy, Equation 7.7: $\mathit{\Delta}_{mix} G = \mathit{\Delta}_{mix} H - T\mathit{\Delta}_{mix} S$ we find that:

$$\mathit{\Delta}_{mix} G = \beta \cdot nRT \cdot \chi_A \chi_B + nRT \cdot (\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$$

where we used Equation 7.10 for $\mathit{\Delta}_{mix} S$. Now we do some factoring and multiply $\beta \cdot nRT \cdot \chi_A \chi_B$ by $(\chi_A + \chi_B)$, which doesn't change anything since the sum of the mole fractions is equal to 1.0: $\mathit{\Delta}_{mix} G = nRT \cdot (\beta \cdot \chi_A \chi_B (\chi_A + \chi_B) + \chi_A \ln(\chi_A) + \chi_B \ln(\chi_B))$

The reason this is done is to create four different terms as shown below:

$$\mathit{\Delta}_{mix} G = nRT \cdot (\ \chi_A \cdot \beta \cdot \chi_B^2 + \chi_B \cdot \beta \cdot \chi_A^2 + \chi\ _A \ln(\chi_A) + \chi_B \ln(\chi_B))$$

When compared to our previous relationship for $\mathit{\Delta}_{mix} G$ based on activity, Equation 7.12, we see that:

As the circled terms must be equal, it must be true that: $\ln(\gamma_A) = beta \cdot \chi_B^2$ and: $\ln(\gamma_B) = \beta \cdot \chi_A^2$, or upon simplification:

$\gamma_A = e^{\beta \chi_B^2}$ and $\gamma_B = e^{\beta \chi_A^2}$

This reveals how the excess enthalpy β factor accounts for Henry's Law from Equation 7.11. To see how, let's say that "A" is our solute and that $P_A = K \cdot \chi_A$. If we divide by P_A^* we find an equation for the activity: $a_A = \left(\frac{P_A}{P_A^*}\right) = \frac{K}{P_A^*} \chi_A$, which is equal to $a_A = \gamma_A \cdot \chi_A = e^{\beta \chi_B^2} \cdot \chi_A$ according to Equation 7.12 and the fact that $\gamma_A = e^{\beta \chi_B^2}$. Consequently, $\frac{K}{P_A^*} \chi_A = e^{\beta \chi_B^2} \cdot \chi_A$ which can be simplified to $K = P_A^* e^{\beta \chi_B^2}$. If we assume $\chi_B \approx 1$ (since "B" is the solvent) then the Henry's Law constant for the solute is:

$$K = P_A^* \cdot e^{\beta}$$

Thus, the excess enthalpy modulates the effective pure partial pressure of solution component "A" when it is in the form of a dilute solute. For the solvent "B", a similar derivation shows $a_B = e^{\beta \chi_A^2} \cdot \chi_B$. However, since $\chi_A^2 \approx 0$, then $e^{\beta \chi_A^2} \approx e^0 = 1$ and the above reduces to: $a_B = \frac{P_B}{P_B^*} = \chi_B$, which is Raoult's Law. Thus, solvents always follow Raoult's Law.

To summarize, the chemical potential of a solution can be known from the same of the vapors in equilibrium. It is tempting to estimate the chemical potential from the composition of the solution. To this end Raoult's Law seems intuitive and sensible, but generally it is a poor approximation. Henry's Law is nothing more than a simple empirical fix to Raoult's Law for highly dilute solutes. Deviations from the ideal or ideal-dilute cases is due to excess enthalpy that either warms or cools a solution after mixing.

7.5: Colligative Properties

Many properties of water are altered when salt is added to it. Specifically, the vapor pressure drops, the freezing point lowers, the boiling temperature rises, and the osmotic pressure increases. One way to remember most of these is to imagine a phase diagram where the triple point is lowered down the solid-gas line while dragging the liquid-gas and solid-liquid borders with it as shown in Fig. 7.5. At a specific temperature, the vapor pressure drop is shown by line A where you can see that the liquid-gas boundary crossing point occurs at a lower pressure. Lines B & C show that, for a given pressure, the solid-liquid and liquid-gas lines cross at different temperatures. This represents the freezing point depression and boiling point elevation.

Here we will use our knowledge of the thermodynamics of mixtures to quantitatively predict these behaviors that are called “colligative properties”. For the most part, the accuracy of these relationships is modest, but they reveal what causes the solvent to react to the addition of a solute. *We will assume that the solutions are ideal, and that all species are at equilibrium from here on.*

7.5.1 Chemical Potentials and Equilibrium. As discussed in the previous section, the change in Gibbs Energy per mole (i.e. the chemical potential) of a liquid is the same as the vapors with which it is in equilibrium. We will use this fact to predict colligative properties. For example, we have already shown how Raoult’s Law is predicated on the lowering of a solvent’s vapor pressure by addition of a solute, specifically in proportion of the liquid state’s mole fraction:

$$P = P^{*} \cdot \chi_{liq} = P^{*} \cdot (1 - \chi_{salt})$$

where χ_{liq} is the mole fraction of liquid water and χ_{salt} is for the added salt. When working on numerical problems related to Raoult’s Law, you must recall that salts disproportionate into two or more species upon dissolution when calculating χ_{salt}. While this one was easy, the changes in phase behavior are more challenging as discussed below.

7.5.1.1 Melting Point Depression. Concerning the lowering of melting point of a solution, we begin by stipulating that both the liquid and solid phases that co-exist in equilibrium must have the same chemical potential:

$$\mu^{\circ}_{solid} = \mu^{\circ}_{liq}$$

where the $^{\circ}$ symbol refers to chemicals in the standard state (25 $^{\circ}$C and 1 bar pressure). From here on we will use an example of adding salt to an equilibrium solution of water with an ice cube (solid water) floating in it. First, the chemical potential of liquid water is lowered by the dissolution of salt as stipulated by Raoult’s Law. Next, the system adjusts to maintain equilibrium, which mathematically means:

$$\mu^{\circ}_{solid} = \mu^{\circ}_{liq} + RT \cdot \ln\left(\chi_{liq}\right)$$

See how the liquid’s chemical potential is lowered on the right yet the ice on the left isn’t affected? This makes sense if the ions do not permeate into the ice, which leaves its chemical potential unaltered.

Recall that the Gibb’s energy of formation per mole is the chemical potential: $\mathit{\Delta}_f G^{\circ}_m = \mu^{\circ}$, and some simple manipulation yields:

\[{\mu }^

ParseError: invalid DekiScript (click for details)

_{fus}G^{{}^\circ }_m=RT\cdot \ln \left({\chi }_{liq}\right) \nonumber \]

where \(-{\mathit{\Delta}}_{fus}G^

ParseError: invalid DekiScript (click for details)

_fG^

ParseError: invalid DekiScript (click for details)

_fG^{{}^\circ }_{liq,m}\) is the change in Gibbs energy per mole for fusion (note that “fusion” is the IUPAC word for melting). The above relationship can be simplified as:

$$\frac{-\mathit{\Delta}_{fus}G^{\circ}_{m}}{RT}=\ln(\chi_{liq}) \tag{7.5.1}$$

Equation 7.5.1 uses the standard state fusion Gibbs energy per mole, which can be found in most thermodynamic data tables. However, Equation 7.15 uses standard state data, so the temperature must be T = 25 $^\circ$C and this is a problem because ice and salty water are not at equilibrium at room temperature! Rather, the temperature should be 0 $^\circ$C or less! Thus, we must use the correct fusion temperature T_{fus} in Equation 7.15, and furthermore the correct thermochemistry data for the change in Gibb’s energy $\mathit{\Delta}_{fus}G_m$ that occurs at the T_{fus} temperature. This is expressed as:

$$\frac{-\mathit{\Delta}_{fus}G_{m}}{RT_{fus}}=\ln(\chi_{liq}) \tag{7.5.2}$$

This equation works just fine, and to demonstrate, pure H_2O water and ice are in equilibrium at 1 bar pressure and 0 $^\circ$C, which means that their chemical potentials are equal:

$$\mu_{solid}-\mu_{liquid}=\Delta_f G_{solid,m}-\Delta_f G_{liq,m}=-\mathit{\Delta}_{fus}G_m=0\ J/mol$$

As a result:

$$\frac{-\mathit{\Delta}_{fus}G_{m}}{RT_{fus}}=0=\ln(\chi_{liq})$$

This is only true if $\chi_{liq}=1$, meaning that the liquid is perfectly pure! Of course it is, since only pure water and ice are at equilibrium at 0 $^\circ$C! If you are confused by the fact that the mole fraction of the liquid is $\chi_{liq}=1$ when there is ice present, this is because the solid ice and liquid water don’t interact very much, and you can say that each has its own mole fraction that is independent of the other. However, when we add salt to the water, then χ_{liq} will go down.

The relationship above allows us to provide a simple thermodynamic explanation for freezing point depression. Adding salt lowers the water’s chemical potential. Ice doesn’t “see” the salt and thus its chemical potential is unaffected, making it appear that there is a problem with maintaining equilibrium via equal chemical potentials. However, chemical potentials are temperature-dependent; thus, the temperature decreases to re-align the chemical potentials of the ice and the salted liquid so that they become equal again. As a result, the freezing point drops.

This leaves us with one final task, which is to derive a quantitative formula for the drop in freezing temperature ΔT as a function of salt content χ_{salt}. As a mathematical description of this process involves changes in salt mole fractions, chemical potentials and temperature, we must use the calculus of derivatives to derive a proper relationship. And although it’s probably confusing just where to start, we do know that adding salt lowers the mole fraction of water (χ_{liq}) and changes the freezing temperature T_{fus}. Consequently, let’s work on $\frac{\partial T_{fus}}{\partial \chi_{liq}}$ and see if we can accomplish our goal with it. However, it turns out that it is much easier solve the inverse relationship $\frac{\partial \chi_{liq}}{\partial T_{fus}}$. To calculate this derivative we can use Equation 7.16: $\ln(\chi_{liq})=\frac{-\mathit{\Delta}_{fus}G_m}{RT_{fus}}$, which means that we are going to solve: $\frac{\partial \ln(\chi_{liq})}{\partial T_{fus}}$ rather than: $\frac{\partial \chi_{liq}}{\partial T_{fus}}$ because these derivative will basically behave the same and it is easy to solve $\frac{\partial \ln(\chi_{liq})}{\partial T_{fus}}$ via the Gibbs-Helmholtz equation:

\[\frac{\partial \ln \left({\chi }_{liq}\right)}{\partial T_{fus}}=\frac{\partial }{\partial T_{fus}}\left(\frac

ParseError: invalid Primary (click for details)

\right)=\frac{1}{R}\frac{\partial \left(\frac

ParseError: invalid Primary (click for details)

\right)}{\partial T_{fus}}=\frac

ParseError: invalid DekiScript (click for details)

\nonumber \]

Here is where this gets interesting; we now integrate this derivative to account for the absolute differences in T_{fus} and χ_{liq} as salt is added by splitting up the partials of $\frac{\partial\ln(\chi_{liq})}{\partial T_{fus}}$ as so:

\[\partial \ln \left({\chi }_{liq}\right)=\frac

ParseError: invalid DekiScript (click for details)

\partial T_{fus} \nonumber \]

The limits of integration allow us to specify an initial temperature and salt concentration, which we will use $\ln\left(\chi_{liq}\right)=0$ for the initial mole fraction (because $\chi_{liq}=1$ for pure liquids) and $T_{fus}=273.15\ K$ for the initial temperature (because the melting temperature of pure water is 0 °C, which is $273.15\ K$). The upper limits of integration are the natural log of the final molar concentration \ln \left({\chi }^'_{liq}\right) and the new melting temperature T^'_{fus}. Starting with the left side:

\int^{ \ln \left({\chi }^'_{liq}\right)}_0{}\partial \ln   \left({\chi }_{liq}\right)= \ln \left({\chi }^'_{liq}\right) \nonumber

We can simplify this result as: \ln \left({\chi }^'_{liq}\right)= \ln \left(1-{\chi }_{salt}\right)\approx -{\chi }_{salt}. And now we integrate the right side:\(\int^{T^'_{fus}}_{T_{fus}}{}\frac

ParseError: invalid DekiScript (click for details)

\partial T_{fus}={\frac

ParseError: invalid Primary (click for details)

]}^{T^'_{fus}}_{T_{fus}}=\frac

ParseError: invalid Primary (click for details)

{T^'_{fus}T_{fus}}\right)=\frac{-{\mathit{\Delta}}_{fus}H_m}{R}\left(\frac{\Delta T}{T^'_{fus}T_{fus}}\right)\)

where T_{fus}-T^'_{fus}=\Delta T. We can make a few simplifications; given the fact that the new melting temperature T^'_{fus} is only slightly less that T_{fus}, then: T^'_{fus}T_{fus}\approx T^2_{fus}. This results in: $frac{-}\mathit{\Delta}_{fus}H_mR\left(\frac{\Delta T}{T^2_{fus}}\right)=-\chi_{salt}$ which rearranges and simplifies to:

$$\Delta T=\frac{R\cdot T^2_{fus}\cdot\chi_{salt}}{\mathit{\Delta}_{fus}H_m} \tag{7.5.3}$$

As you work some practice problems using Equation 7.17, you will find that it is decently accurate but not perfect. This clearly has to do with the approximations made in the derivation, such as the use of Raoult's Law and especially the fact that we did not account for the temperature dependence of $\mathit{\Delta}_{fus}H_m$ when analyzing the \(\int^{T^'_{fus}}_{T_{fus}}{}\frac

ParseError: invalid DekiScript (click for details)

\partial T_{fus}\) integral. Regardless, the relationship reveals some interesting phenomena, such as the fact that the freezing point depression is inversely proportional to the enthalpy of fusion. If the enthalpy is high for a liquid, then the effect of salt is minimized. Also, the freezing point depression of water is enhanced by adding salts such as $CaCl_2$ due to the large number of dissociated ions that increases χ_{salt}; this information helps with managing roadways during winter weather.

7.5.1.2 Boiling point elevation. Essentially the same derivation is used to calculate the increase in boiling point of a salty solution, and as a result we won't repeat the effort here. The relationship is: $\Delta T = \frac{RT_{vap}^2 \cdot \chi_{salt}}{\Delta_{vap} H_m}$

where the relevant change is vaporization and {\Delta T=T^'_{vap}-T}_{vap}, the opposite order that appeared in the freezing point depression problem.

7.5.1.3 Osmotic Pressure. Living cells have osmotic pressure, which is to say that they experience a higher internal pressure than atmospheric resulting from the fact that the cells' cytoplasm contains dissolved salts and other biologicals such as proteins. Osmotic pressure can be measured using a system such as that shown in Figure 7.6, whereby a saltwater solution (left) is vertically displaced upwards in a column by pressure. This "push" experienced by the left side is generated by osmosis from pure water on the right side that is separated by a semi-permeable membrane. The osmotic pressure $\mathit{\Pi}$ is equal to the applied pressure necessary to even out the liquid column levels.

Here we seek to explain exactly why this osmotic pressure differential exists and how to calculate $\mathit{\Pi}$. There are two simple explanations; one is that the pure water on the right side of Figure 7.6 is attempting to dilute the salty water on the left, which is an action to resist change (basically a Le Chatelier-type process). A better thermodynamic argument stipulates that the chemical potential of the salty water is less than the pure water, and as such the pure water moves towards it. This "push" of the pure water into the diluted water occurs until equilibrium is reached, at which point the chemical potentials of the salt water and pure water are equal. However, there is a problem with the application of Raoult's Law due to the fact that the chemical potential of the saltwater solution on the left: $\mu^\circ + RT \cdot \ln(\chi)$ is supposed to be equal to the chemical potential of pure water on the right μ°:

$$\mu^\circ + RT \cdot \ln(\chi_{liq}) = \mu^\circ$$

This equation is true only if $\chi_{liq} = 1$, but when we add salt to the water then $\chi_{liq} < 1$. Clearly we are missing some extra source of chemical potential, which in fact comes from osmotic pressure. Recall that the chemical potential is the Gibbs energy per mol which changes as:

$$\partial\mu = \partial G_m = -S_m \partial T + V_m \partial P$$

At constant temperature the chemical potential changes with pressure as: $partial\mu = V_m \partial P$. If we integrate this simple relationship: $\Delta\mu = \frac{V}{n_{water}} \Delta P$, where the change in pressure ΔP the osmotic pressure Π. We apply this osmotic pressure correction to the saltwater solution to the left side the result is $\mu^\circ + RT \cdot \ln(\chi_{liq}) + \mathit{\Pi} \frac{V}{n_{water}}$, which we equate to the chemical potential of the pure water on the right side as:

$$\mu^\circ + RT \cdot \ln(\chi_{liq}) + \mathit{\Pi} \frac{V}{n_{water}} = \mu^\circ$$

Some cancellation and algebraic simplification yields:

$$\mathit{\Pi} \frac{V}{n_{water}} = -RT \cdot \ln(\chi_{liq})$$

As χ_{liq} is the mole fraction of the water solvent and $\chi_{liq} = 1 - \chi_{salt}$, we can apply the approximation: $\ln(\chi_{liq}) = \ln(1 - \chi_{salt}) \approx -\chi_{salt}$. Inserting this into the relationship above: $\mathit{\Pi} V = n_{water} RT \cdot \chi_{salt}$

Now we make one last approximation, which is that: $\chi_{salt} = \frac{n_{salt}}{n_{water} + n_{salt}} \approx \frac{n_{salt}}{n_{water}}$. This is reasonable so long as $n_{salt} \ll n_{water}$. This approximation can be inserted this into the expression for osmotic pressure: $\mathit{\Pi} V = n_{water} RT \cdot \chi_{salt} = n_{water} RT \cdot \frac{n_{salt}}{n_{water}} = n_{salt} RT$

Finally, we have a familiar-looking relationship:

$$\mathit{\Pi} V = n_{salt} RT \tag{7.5.4}$$

Note that the appearance to the perfect gas law is purely coincidental, but it does help making the osmotic pressure formula easier to remember.

Conclusion. In this chapter we introduced the concepts of thermodynamics in condensed phases, which is to say that we hijacked gas phase equations from earlier chapters and used the chemical potential as a conduit to the thermodynamics of the condensed phase. Raoult’s Law was used to predict how the vapor phase is connected to the contents of the liquid mixture from which it originates, and we were able to use it to demonstrate colligative properties. In reality Raoult’s Law works well for solvents; however, most systems do not follow it. Henry’s Law is a “fix it” for solutes, and when it doesn’t work then we turn to activity. Activity is roughly proportional to concentration, although it has no units and is designed to make our thermodynamic equations work. In the next chapter we will make use of these concepts for further examinations of different phases, which will allow us to calculate phase diagrams including systems with more than one component.

CHAPTER OVERVIEW

8: Phase Changes

Phase diagrams show under what conditions that one or more chemical substances exist in the solid, liquid or vapor state. There are multiple ways to express this information, although usually such diagrams take the form of 2D graphs where different phases appear as interior regions and thermodynamic variables are along the axes. Shown in Figure 8.1 is a common and rather generic example of a pressure vs. temperature phase diagram for a single chemical. We will start to develop our understanding of phase equilibria as a function of pressure and temperature because these are intensive variables that define equilibrium. We also assume that phase diagrams always represent systems at equilibrium, although you should know that it is possible to have chemicals exist in a non-equilibrium phases albeit for a short period of time. For example, the present record on the coldest temperature of liquid water is -45 $^\circ$C!1,2

The phase diagram in Figure 8.1 shows the the usual players: solid, liquid and gas, as well as an additional curious thing called the “supercritical”. This is a phase that is like a combination of liquid and gas. There are broad areas that represent each phase, lines that delineate between them, and a single triple point between all three phases. There can be other triple points, and these may occur in the solid phase region area. This is possible because there can be more than one solid phase as defined by different crystallographic structures. For example, water is known to have 9 different solid phases. There is of course only one gas and liquid phase with one exception, that being the case of helium that can have two liquid phases due to the formation of a “Bose-Einstein condensate”, which is an esoteric quantum mechanical phenomenon. As shown in Figure 8.1, the liquid-solid line slopes to the right, which means that if you increase the pressure of a solid then it will melt at a higher temperature. This is because most things have a denser solid phase compared to the liquid, so the application of high pressure inhibits the expansion of the solid into the liquid phase. Water is a notable exception due to the fact that it has a less dense solid phase. You know this already because you are well aware that ice floats in water. As a result, the phase diagram of Figure 8.1 does not apply to water, which is shown in Figure 8.2.

As discussed in the previous chapter on colligative properties, a phase diagram is more information rich than it initially appears. For example, in Figure 8.1 we plot a point at 1 bar pressure at 25 $^\circ$C where we see that this chemical is a liquid. A line runs parallel along the x-axis (temperature) to the left and right of that point and is constant along the y-axis (1 bar pressure). The line crosses the solid-liquid boundaries, and where this crossing occurs can be used to read off the melting point (T_{fus}) and boiling point (T_{vap}). Looking back at the point at 1 bar, 25 $^\circ$C in Figure 8.1 we see a line that points straight down and intersects the liquid-gas boundary. This point provides the pure partial vapor pressure of this substance in equilibrium with the liquid as measured at 1 bar pressure. We used this value in our Raoult’s Law calculations in the previous chapter.

The phase diagram of water in Figure 8.2 shows a solid-liquid line that slopes to the left due to the unusual lower density of the solid state compared to the liquid. This phase diagram also demonstrates why you have to cook Raman noodles longer at higher altitudes; if you go up in altitude and experience a lower atmospheric pressure, then the boiling temperature decreases. For example, water boils at 94.6 ºC in Albuquerque, New Mexico.

8.1: The Gibbs Phase Rule

In the following sections we will develop various thermodynamic relationships to mathematically "create" a phase diagram, although we have to have some data such as the location of the triple point. We can also show that there cannot be such a thing as a quadruple point, unless the phase diagram has more than one component (i.e. its for a mixture). This can be demonstrated by calculating the number of degrees of freedom of the phase diagram; note this is not the same "degrees of freedom" of a gas molecule that was discussed in Chapter 2. Here we will define what a degree of freedom is by example; if we have a P vs. T diagram, we automatically have two degrees of freedom, which are pressure and temperature. With these two degrees of freedom we may be able to change pressure and temperature independently of each other and remain in a particular state. In plain English, we can heat or cool water a few degrees and still have liquid water, even if we are at a higher or lower pressure altitude (i.e. Death Valley vs. Mexico City).

Of course, if we keep heating the water eventually it will start to boil; at this point we say that the liquid water and steam co-exist. If we increase the temperature further then all the liquid boils off. In contrast, if we wish to maintain the liquid-gas equilibrium at the higher temperature, we can do so by simultaneously increasing the pressure as dictated by the line between the two phases seen in Figures 8.1 and 8.2. This means that pressure is no longer a degree of freedom because it must change in a way that is uniquely determined by the temperature according to the phase diagram. Of course, we can also state that if we change the pressure then we don't have control over the temperature. It doesn't really matter because, in either case, we only have one degree of freedom if we are trying to maintain equilibrium between two phases.

Let's put this discussion into mathematical terms. We start by stating that the number of degrees of freedom in a phase diagram, "f", is at least equal to 2 to represent temperature and pressure: $f \;=\; 2$. There could be more than one component "c" present. For example, perhaps we are attempting to describe the phase diagram of an ethanol + water mixture. In this case, we are free to decide on how much of each component to add to the diagram, giving us "c" more degrees of freedom. Thus, $f \;=\; 2 \;+\; c$. If there are "p" number of phases present, then we have even more degrees of freedom. For example, let's say that we wish to drop in an ice cube (solid) into our ethanol + water liquid mixture, in which we can decide how much ice to add which is a degree of freedom. Consequently, we have $c \cdot p$ degrees of freedom in addition to temperature and pressure, and thus the total is $f \;=\; 2 \;+\; c \cdot p$.

However, we have run into a small problem. If we have a one phase system ($p = 1$) composed of two liquid components ($c = 2$), then is it really true that we have 2 additional degrees of freedom aside pressure and temperature? Oddly no, because the system can be characterized by just one variable, which is the percent composition of just one component. For example, in our ethanol + water solution the composition can be known just by the water mole fraction (χ_{water}) because the ethanol composition is automatically: $\chi_{EtOH} = 1 - \chi_{water}$. Thus, there is just one degree of freedom. Let's use some mathematical representations to understand this in a better and more general way. If we have c components, then it must be true that the sum of their mole fractions is 1:

$$\chi_1 + \chi_2 + \chi_3 + \ldots \chi_c = 1$$

This equation represents a loss of a degree of freedom, because you have no choice that the sum of mole fractions is 1. There has to be an equation like this for each phase:

$$\begin{gathered}\chi_1^\alpha + \chi_2^\alpha + \chi_3^\alpha + \ldots \chi_c^\alpha = 1 \\ \chi_1^\beta + \chi_2^\beta + \chi_3^\beta + \ldots \chi_c^\beta = 1 \\ \ldots \\ \chi_1^p + \chi_2^p + \chi_3^p + \ldots \chi_c^p = 1\end{gathered}$$

where α, β refer to "p" different phases, like solid, liquid, or vapor. This is necessary because, as we showed in the previous chapter, the compositions of each phase do not have to be equal to each other. Given the above it is clear that there are "p" number of equal signs due to this mole fraction restriction, so we must subtract "p" from the degrees of freedom:

$$f \;=\; 2 \;+\; cp \;-- p$$

At this point a rule for the "degrees of freedom" game has been revealed: add the degrees of freedom to "f" but subtract the number of equal signs from constraining equations. In terms of constraints, there is an additional one aside the need for mole fractions to sum properly. This is the fact that, at equilibrium, the chemical potentials of the different components in the different phases must be equal as we showed in C. For example, for water in equilibrium with ice it must be true that:

$$\mu^{\alpha} = \mu^{\beta}$$

(α=liquid, β=ice). This equation represents a constraint that results in further reductions to the degrees of freedom. And while it appears we have $(p-1)$ such number of equal signs, however there may be other components in difference phases. As shown below, there are c equations that have $(p-1)$ equal signs:

$$\mu_1^{\alpha} = \mu_1^{\beta} = \ldots \mu_1^{p} \mu_2^{\alpha} = \mu_2^{\beta} = \ldots \mu_2^{p}$$

$$\ldots \mu_c^{\alpha} = \mu_c^{\beta} = \ldots \mu_c^{p}$$

Consequently the number of constraining equations is $c \cdot (p-1)$. Thus we now have:

$$f = 2 + cp - p - c \cdot (p-1)$$

A little algebra shows that:

$$f = 2 + c - p \tag{8.1.1}$$

which is known as the **Gibbs phase rule**.

Let's work a few examples. If we are characterizing a single phase of one component in a phase diagram, then the number of degrees of freedom is: $f = 2 + c - p = 2 + 1 - 1 = 2$, which are pressure and temperature. In a phase diagram such as shown in Figure 8.1, only an open (or "flat") region can represent 2 degrees of freedom. In contrast, for two equilibrium phases of a single component the number of degrees of freedom are: $f = 2 + c - p = 2 + 1 - 2 = 1$. In a phase diagram of Figure 8.1, a single degree of freedom must be represented by a solid line because lines have a single independent variable and a corresponding dependent variable. These are why the co-existence of solids and liquids, solids and gases, and liquids and gases are represented by lines in the P vs. T phase diagrams in Figures 8.1 and 8.2. Coexistence of three phases can only be represented by a point, because a point has no degrees of freedom ($f = 0$); this is the triple point. There is no such thing as a quadruple point in a single component phase diagram, because there cannot be negative degrees of freedom.

8.2: Entropy is the Reason Phase Changes Occur

In Sec. 5.3.3, we showed you that, at constant pressure, Gibbs energy always decreases with temperature. We will derive that again here, starting with the change in Gibbs energy per mole which is the chemical potential:

$$\partial G_m = \partial\mu = -S_m \partial T + V_m \partial P$$

Taking the derivative with respect to temperature at constant pressure results in:

$$\left(\frac{\partial\mu}{\partial T}\right)_P = -S_m \tag{8.2.1}$$

The relationship above reveals that $\left(\frac{\partial\mu}{\partial T}\right)_P$ is always negative because entropy per mole is always positive. Thus, the chemical potential of a particular phase of a substance decreases with temperature in proportion to that phase's entropy. Consequently, heating causes the chemical potential of a liquid decreases faster than a solid. Likewise, the chemical potential of a gas decreases faster than the liquid. This is important because, at very low temperatures, the solid phase has the lowest chemical potential. If you doubt this, we remind you that all chemicals are solids at very low temperatures. As the temperature increases, the liquid's chemical potential eventually becomes lower than the solid's, and thus we observe a phase transition (melting) at that temperature. As the temperature increases further, eventually the gas phase's chemical potential becomes lower than the liquid's which is why we observe boiling. This is all represented in Figure 8.3 (left-most figure); note that chemical potential is shown decreasing linearly with temperature but this is just an approximate representation.

As for the effect of pressure at constant temperature, we use the change in Gibb's energy: $\partial G_m = \partial\mu = -S_m \partial T + V_m \partial P$ to show that:

$$\left(\frac{\partial\mu}{\partial P}\right)_T = V_m \tag{8.2.2}$$

Equation 8.2.2 is always positive because volume per mole can only be positive. And usually a solid is denser than the liquid, both of which are always denser than the gas. When we combine these effects in Figure 8.3, we can start to map out the pressure and temperature points of coexistence between two phases on a P vs. T phase diagram.

We hope the discussion thus far has aided your understanding of phase transitions; however, we can't actually use equations 8.2 or 8.3 to define the boundaries in a phase diagram such as that shown in Figure 8.1. This can be accomplished by numerically calculating the chemical potentials of all phases over the full range of pressures and temperatures in the graph and determining where they are equal. And since we never know what the absolute energies are, we must always use relative formation energies ($\Delta_f G_m$) when performing thermochemical calculations. The $\Delta_f G_m$'s are chemical potentials, and we must adjust the standard state values from a data table for other pressures and temperatures. To this end we use the many tools discussed in Chapter 6 that provided for us the following:

$$\mu(P,T) = \Delta_f G_m(P,T) = \Delta_f H_m(P,T) - T \times \Delta_f S_m(P,T)$$

where:

$$\Delta_f H_m(P,\ T) = \Delta_f H_m^\circ + \int_{298.15K}^{T} C_{P,m}(T)\,\partial T$$

and:

$$\Delta_f S_m(P,T) = \Delta_f S_m^\circ + \int_{298.15K}^{T} \frac{C_P(T)}{T}\partial T - \int_{1bar}^{P} \frac{V_m}{T}\partial P$$

The phase boundaries occur where $\mu^{solid} = \mu^{liquid}$, $\mu^{liquid} = \mu^{gas}$ and $\mu^{solid} = \mu^{gas}$. Furthermore, the phase present is the one with the lowest chemical potential for any given P and T in the phase diagram. This approach is demonstrated for water in Figure 8.4, where we have made 2-dimensional plots of the chemical potential surfaces of each water phase including projections where the energies cross onto the P vs. T planes. These clearly mark the boundaries between phases with considerable accuracy. As shown in Figure 8.4 A, the solid – liquid chemical potentials are equal at 0 °C at 1 bar pressure, and the equilibrium is left-sloping with increasing pressure due to the lower density of ice compared to the liquid. Figure 8.4 B shows that the liquid water – steam boundary begins at 373 K at 1 bar pressure and has a boiling temperature that rises with pressure. Unfortunately, calculations of this nature are extremely labor intensive, and require accurate knowledge of the temperature dependence of the heat capacities of all the phases. One can get lost in all the equations and calculations, making it is difficult to discern if there are simple reasons for why a phase diagram appears the way it does. This prompts us to use a more simple approach.

8.2.1 The Clausius-Clapeyron Relation

In our discussion above we calculated where two phases α and β are in equilibrium by finding the pressure and temperature points where their chemical potentials are equal: $\mu^\alpha = \mu^\beta$. Another rule of thermodynamics requires that the derivatives of the chemical potentials are also equal at equilibrium: $\partial\mu^\alpha = \partial\mu^\beta$. In a constant pressure and temperature world this means:

$$-S_m^\alpha \partial T + V_m^\alpha \partial P = -S_m^\beta \partial T + V_m^\beta \partial P$$

Collecting like terms:

$$V_m^\alpha \partial P - V_m^\beta \partial P = S_m^\alpha \partial T - S_m^\beta \partial T$$

Next we factor the change in pressure and temperature and divide the results:

$$\left(V_m^\alpha - V_m^\beta\right)\partial P = \left(S_m^\alpha - S_m^\beta\right)\partial T$$

$$\frac{\partial P}{\partial T} = \frac{\left(S_m^\alpha - S_m^\beta\right)}{\left(V_m^\alpha - V_m^\beta\right)} = \frac{\Delta S_m}{\Delta V_m} \tag{8.2.3}$$

Since we don't like to work with changes in entropy due to the complexity of entropy in general, we can make a clever substitution. Since enthalpy represents a heat exchange with the outside ($\partial H = \partial q$), and given the definition of a change in entropy ($\partial S = \frac{\partial q}{T}$), we can substitute \(\frac{\Delta H_m}{T})for ΔS_m to show:

$$\frac{\partial P}{\partial T} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \cdot \Delta V_m} \tag{8.2.4}$$

This is the Clausius-Clapeyron equation that can help predict where different phases co-exist on a P vs. T phase diagram. Below, we use equation 8.5 to directly map out the lines between solid-liquid, solid-gas, and liquid-gas boundaries in a phase diagram.

8.2.1.1. Solid-Liquid

We will begin by analyzing the relationship between the solid and liquid phases, which allows us to determine melting temperature of a substance at different pressures. Since we are discussing the process of melting ΔH_m in Equation 8.2.4 is specifically the enthalpy of fusion:

$$\Delta H_m = \Delta_{fus} H_m = \Delta_f H_{m,liquid} - \Delta_f H_{m,solid}$$

Likewise:

$$\Delta V_m = \Delta_{fus} V_m = V_{m,liquid} - V_{m,solid}$$

To derive the P vs. T lines of equilibrium, we take the Clausius-Clapeyron relation (Equation 8.2.4) and "juggle" the partials as so:

$$\partial P = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \frac{\partial T}{T}$$

Note that we can make the approximation that nether the enthalpy nor the density are temperature dependent, which is not correct. However, inclusion of the temperature dependence of these properties creates a nightmarish calculus scenario, so we will approximate that there is no temperature dependence. As a result, the integration of the above is simple:

$$\int_{P_1}^{P_2} \partial P = P_2 - P_1 = \int_{T_1}^{T_2} \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \frac{\partial T}{T} = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \int_{T_1}^{T_2} \frac{\partial T}{T} = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \ln\left(\frac{T_2}{T_1}\right)$$

Here we see that a starting point on the phase diagram, (P_1, T_1) must be known before we can determine the pressure and temperature of the solid-liquid line of coexistence at a different condition (P_2, T_2). Clearly the triple point is a good choice, and thus $P_1 = P_t$ and $T_1 = T_t$. We will simply call P_2 and T_2 as P and T in our simplification of the above equation:

$$P = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \ln\left(\frac{T}{T_t}\right) + P_t \tag{8.2.5}$$

Equation 8.2.5 gives us a formula for a line that delineates between the liquid and solid phases in a phase diagram.

Does Equation 8.2.5 conform with the experimental data? First note that natural logarithms are fairly linear, and as a result Equation 8.2.5 is like a line with a slope of $\frac{\Delta_{fus} H_m}{\Delta_{fus} V_m}$. Concerning the slope, the numerator $\Delta_{fus} H_m$ (the input of energy required to melt the solid) is usually a rather large, positive value. At the same time, the difference in the densities of solids and liquids is very small and as a result the slope of the solid-liquid line $\frac{\Delta_{fus} H_m}{\Delta_{fus} V_m}$ is huge. Concerning the right or leftwards slant of Figures 8.1 and 8.2, respectively, $\Delta H_{m,fus}$ doesn't play a role since it is always positive. In contrast, the volume per mole in the denominator is generally greater for a liquid than a solid. This makes $\Delta V_{m,fus}$ likewise positive, which is why the P vs. T line between the solid and liquid phases is to the right in Figure 8.1. The notable exception is water, which has a denser liquid than the solid (remember ice cubes float) and thus $\Delta V_{m,fus}$ is negative. As a result, water's solid-liquid line is to the left as seen in Figure 8.2.

8.2.1.2. Solid-Vapor

A solid can evaporate directly into the vapor phase, which is the process of sublimation. Here we use the Clausius-Clapeyron relation as previously to define the solid-vapor boundary:

$$\partial P = \frac{\Delta_{sub} H_m}{T \cdot \Delta_{sub} V_m} \partial T$$

where $H_{m,sub} = H_{m,vap} - H_{m,solid}$ and $\Delta V_{m,sub} = V_{m,vap} - V_{m,solid}$. We will assume that enthalpy is independent of temperature, but we cannot do the same for $\Delta V_{m,sub}$ as a gas's volume is highly dependent on the temperature. In fact, we can deal with this temperature dependence by making a minimal approximation whereby the difference in molar volume (gas – solid) can be assumed to just be the molar volume of the gas: $\Delta V_{m,sub} \approx V_{m,vap}$ and thus $\partial P = \frac{\Delta_{sub} H_m}{T \cdot V_{m,vap}} \partial T$

This works because the volume of a gas is always significantly greater than that of the solid. We can make another substitution into the above by inserting the perfect gas law $V_m = \frac{RT}{P}$ to substitute $V_{m,vap}$:

$$\partial P = \frac{\Delta_{sub} H_m}{T\left(\frac{RT}{P}\right)} \partial T = \frac{P \cdot \Delta_{sub} H_m}{RT^2} \partial T$$

The pressure factor must be moved from the left side before integration, and as before we will assume that the initial pressure and temperature are those of the triple point:

$$\int_{P_t}^{P} \frac{\partial P}{P} = \ln\left(\frac{P}{P_t}\right) = \int_{T_t}^{T} \frac{\Delta_{sub} H_m}{RT^2} \partial T = \frac{-\Delta_{sub} H_m}{R}\left(\frac{1}{T} - \frac{1}{T_T}\right)$$

Some rearrangement makes this easier to look at:

$$\ln(P) = \frac{-\Delta_{sub} H_m}{RT} + C \tag{8.2.6}$$

where the constant is $C = \frac{\Delta H_{m,sub}}{RT_t} + \ln(P_t)$. Equation 8.2.6 looks like an exponential rise in a graph of P vs. T, which is exactly how the solid-vapor line appears in the phase diagram examples shown in Figure 8.1 and 8.2.

8.2.1.3. Liquid-Vapor

The development of the liquid-vapor line is identical to the above, except the process is vaporization rather than sublimation:

$$\ln\left(\frac{P}{P_t}\right) = \frac{-\Delta_{vap} H_m}{R}\left(\frac{1}{T} - \frac{1}{T_T}\right)$$

which as before can be rearranged into: $\ln(P) = \frac{-\Delta_{vap} H_m}{RT} + C$ where $C = \frac{\Delta H_{m,vap}}{RT_T} + \ln(P_t)$. As in the previous example, the liquid-vapor line appears as an exponential rise starting from the triple point just as seen in Figures 8.1 and 8.2.

8.3: Other Examples of Phase Changes

Talking about ice melting is about as fun as watching paint dry, which is itself a phase change. However, there are many interesting things about phase changes once one realizes how many different types of phase changes exist. For example, surfactants such as phospholipids can lie flat on the surface of water, until they are pressurized upon which they stand up. This is important for living cells that are coated with phospholipids. Solid state materials have different magnetic phases; another example of a phase change is cooling a ceramic to the electrically superconducting state. We know that these are legitimate phase changes by noting discontinuities with thermodynamic variables such as heat capacity upon heating, as energy is inputted with no observable change in temperature. In the next few sections we review some other examples of interesting phase diagrams for multicomponent systems, which explain why solder (i.e. wire glue) melts at a relatively low temperature.

Multicomponent Phase Diagrams, pressure vs. composition

Mapping the phases of solutions is important for understanding many processes such as separation via distillation, an example we will study in this section. Distillation requires us to understand the liquid-vapor phase diagram, and we will stipulate that the vapor originates from a liquid that is an ideal solution. The phase diagram itself reveals the liquid and vapor phases as a function of pressure (y axis) and composition (x axis, in the form of the mole fraction). To create this phase diagram we will make a plot of total pressure vs. liquid phase composition using Raoult's Law, Equation 7.2 from the previous chapter. If you don't recall, Raoult's Law relates a component's vapor partial pressure to its mole fraction in the liquid state; for example: $P_B = \chi_B P_B^*$ where P_B^* is the pure partial pressure for the B component. We must use this information to determine the net pressure P, which we can do simply by adding the individual partial pressures:

$$P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^*$$

Since $\chi_A = 1 - \chi_B$ and:

$$P = P_A + P_B = (1 - \chi_B)\, P_A^* + \chi_B P_B^*$$

then:

$$P = P_A^* + \chi_B \left(P_B^* - P_A^*\right)$$

This relationship is plotted in Figure 8.5, which is clearly a simple line. Now, we must determine the total pressure as a function of the composition of the vapor phase using the mole fractions of the vapors υ_A and υ_B (note we use χ's to refer to the liquid, and υ's for the vapors). It may seem odd that we are introducing a new variable for the vapor phase mole fractions; afterall doesn't Raoult's Law mean $\chi_A = \upsilon_A$ and $\chi_B = \upsilon_B$? No, it doesn't; this is because Raoult's Law relates a component's liquid mole fraction to its vapor partial pressure, not the contribution to the total pressure. For example, imagine that the pure partial pressure of a liquid is 0 Pa. In this case, the mole fraction of the liquid (χ) doesn't have any effect on the total pressure and is thus unrelated to the vapor's υ! To demonstrate using equations, first note that the mole fraction of a vapor is related to the pressure and pure partial pressure via Dalton's Law: $P_B = \upsilon_B P$ which rearranges to:

$$\upsilon_B = \frac{P_B}{P} = \frac{P_B}{P_A^* + \chi_B \left(P_B^* - P_A^*\right)} = \frac{\chi_B P_B^*}{P_A^* + \chi_B \left(P_B^* - P_A^*\right)}$$

where we used the fact that $P = P_A^* + \chi_B \left(P_B^* - P_A^*\right)$ and $P_B = \chi_B P_B^*$. A similar derivation for component "A" yields:

$$\upsilon_A = \frac{\chi_A P_A^*}{P_B^* + \chi_A \left(P_A^* - P_B^*\right)}$$

From here we see that, if $P_B^* = P_A^*$, then $\upsilon_B = \chi_B \frac{P_B^*}{P_A^*}$ and $\upsilon_A = \chi_A \frac{P_A^*}{P_B^*}$. Consequently, it is immediately obvious that the mole fractions in the liquid and vapor phases are not exactly equal; furthermore, these relationships are even more complex if $P_B^* \neq P_A^*$.

To complete a pressure vs. composition phase diagram, we have to determine the total pressure as a function of the vapor mole fractions υ_A and υ_B. First, we solve the liquid mole fractions as functions of the vapor mole fractions using the relationships above, which are:

$$\chi_A = \frac{\upsilon_A P_B^*}{P_A^* - \upsilon_A \left(P_A^* - P_B^*\right)} = \frac{\upsilon_A P_B^*}{P_A^* - (1 - \upsilon_B)\left(P_A^* - P_B^*\right)} = \frac{\upsilon_A P_B^*}{P_B^* - \upsilon_B \left(P_B^* - P_A^*\right)}$$

where we used $\upsilon_A = (1 - \upsilon_B)$, and:

$$\chi_B = \frac{\upsilon_B P_A^*}{P_B^* - \upsilon_B \left(P_B^* - P_A^*\right)}$$

When we plug these into the expression for total pressure $P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^*$ we find:

$$P = \frac{\upsilon_A P_B^* P_A^*}{P_B^* - \upsilon_B \left(P_B^* - P_A^*\right)} + \frac{\upsilon_B P_B^* P_A^*}{P_B^* - \upsilon_B \left(P_B^* - P_A^*\right)} = \frac{\left(\upsilon_A + \upsilon_B\right) P_A^* P_B^*}{P_B^* - \upsilon_B \left(P_B^* - P_A^*\right)} = \frac{P_A^* P_B^*}{P_B^* - \upsilon_B \left(P_B^* - P_A^*\right)}$$

This behavior is illustrated in Figure 8.6 for the case of $P_B^* \gg P_A^*$.

With the total pressure expressed as a function of the liquid and vapor mole fractions (Figures 8.5 and 8.6), we can now generate the multicomponent liquid-vapor phase diagram by the simple superimposition of these two graphs as shown in Figure 8.7. This multicomponent phase diagram has a single y axis (total pressure) yet two simultaneous x axes, that being χ_B and υ_B. Instead of a line between the liquid and vapor (gas) phase found in a single component phase diagram (Figures 8.1 and 8.2), we see instead a liquid + vapor region. The reason that the equilibrium between these phases has gone from a line in a single component phase diagram to an area in the multicomponent one is because there are two degrees of freedom as verified by the Gibbs Phase rule $f = 2 + c - p = 2 + 2 - 2 = 2$. Recall that there is only one degree of freedom in a single component diagram.

To understand the data presented in Figure 8.7, we will study the same diagram over a closer range with points defined within each region as shown in Figure 8.8. The first point, x_1, is at high pressure. Here, the system is in a single liquid state with a composition that can be read off the x-axis as $\chi_B = 0.6$ (obviously this makes $\chi_A = 0.4$). This is the "boring" part of the diagram; however, if we decrease the total pressure we arrive at point x_2 which is more interesting as two phases are present. Each phase, liquid and vapor, has its own compositions that are determined by drawing tie lines to the left and right of the x_2 point to the liquid line (blue) and vapor line (red), respectively, as seen in Figure 8.8. This shows that the vapor is composed of mostly "B" ($\upsilon_B = 0.7$, $\upsilon_A = 0.3$) and likewise the liquid is mostly "A" ($\chi_B = 0.33$, $\chi_A = 0.67$). The reason that the compositions of the vapor and liquid differ within the liquid + vapor region of Figure 8.8 is because component "B" vaporizes more readily than "A" due to the former's higher vapor pressure. And since "B" has been removed from the liquid, the remainder is richer in component "A". If we lower the pressure further to arrive at x_3 the pressure is low enough such that both liquids have fully vaporized.

8.3.1.1. The Lever Rule

The multicomponent phase diagram in Figure 8.8 is more information rich than it appears and imparts an interesting lesson on degrees of freedom. Imagine that the system is in a state described by point x_2. Next, you add a small additional amount of liquid "B" and allow the system to re-equilibrate; what do you think is different? Probably you believe that the percentage of "B" in the liquid's composition has increased. However, this is not the case, mostly because addition or subtraction of a small quantity of a component isn't an available degree of freedom. This is because at point x_2 there are $f = 2 + c - p = 2 + 2 - 2 = 2$ degrees of freedom which are the temperature and pressure. As a result, the addition of a small quantity of "B" cannot change the composition of either the liquid or vapor in the system. In fact, given that temperature is constant the only way to increase the "B" in the liquid phase's composition is to raise point x_2, i.e. increase the pressure. To summarize, if the pressure and temperature are unaltered after adding or removing a small quantity of either "B" or "A", then the compositions of the liquid and vapor phases are unaltered.

So in this example where did the extra "B" go? The answer is that the excess "B" must be accounted for by an increase in the phase rich in "B", which is the vapor. Thus, when you poured in more liquid "B" into the system, it reached equilibrium by creating more vapor. This allows the system to absorb the mass yet leave the compositions of both the liquid and vapor phases unaltered. The phase diagram is even capable of quantifying the relative amounts of liquid and vapor using the following method. At point x_2, we already discussed how tie lines to the left and right allow us to determine the phases' compositions. If we call the length of the tie lines I_{liq} and I_{vap}, then the relative masses of liquid and vapor are related via:

$$\frac{I_{liq}}{I_{vap}} = \frac{m_{vap}}{m_{liq}}$$

where m_{liq} and m_{vap} is the mass of "A" and "B" in the liquid and vapor phases, respectively. Consequently, one can see that if more "B" is poured into the system at state x_2, then point x_2 would shift to the right resulting in a larger I_{liq}, smaller I_{vap}, and thus a greater amount of vapor. As in our initial discussion on single component phase diagrams, it appears that there is much greater information "hidden" in these diagrams than initially appears!

8.3.1.2. Temperature vs. composition, distillation and azeotropes. The case of vapor-liquid phase diagrams

It is possible to create multicomponent phase diagrams as a function of temperature at a constant pressure. In fact, these are more practical because they help us understand such processes as distillation. Shown in Figure 8.9 is a temperature vs. vapor + liquid mole fraction diagram for a mixture of water and ethylene glycol at a constant pressure of 100 kPa ($\sim$1/3 an atm). The graph makes it clear that there is only a vapor at a high temperature while only one liquid phase exists at a low temperature, as is sensible. Also, the pure liquid boiling points can be read off the right and left sides of the graph, and we sensibly see that water's boiling point is lower than 100 $^\circ$C given the reduced pressure. Most importantly, the graph reveals the existence of a mixed phase state at intermediate temperatures.

To understand how to use the multicomponent phase diagram fully we examine Figure 8.9 starting at point x_1. Here, there is a single liquid phase composed of 50% / 50 % ethylene glycol and water. If we raise the temperature to point x_2, there remains a liquid with a composition of $\sim$93% ethylene glycol and a vapor that is $\sim$30% water. The vapor and liquid are of course the same temperature, and the reason that the vapor has more water is because H_2O has a lower boiling point than ethylene glycol. Now imagine that the vapor could be collected and cooled back into a liquid, and re-vaporized again. If we did so we would be at point x_3, then the vapor would nearly be pure water. If we repeat this cycle several more times, it seems that we could capture nearly pure water via the vapor phase while leaving behind a pure ethylene glycol liquid phase, given that all the water eventually vaporizes out. This process is distillation as guided by the large arrows in Figure 8.9.

Two phase diagrams of azeotropic liquid mixtures are shown in Figures 8.10. An azeotrope is made from a non-ideal liquid mixture, imparting a strikingly different phase behavior compared to the previous example. In Figure 8.10 A we see an example of a positive azeotrope, methanol and chloroform, that has a lower boiling point when mixed comparted to either individual liquid. A negative azeotrope such as formic acid in water has a higher boiling point as a mixture as shown in Figure 8.10 B. As part of an exercise at the end of the chapter, you will demonstrate that these systems cannot be fully purified via distillation.

8.3.1.4. Liquid-liquid phase diagrams

It may surprise you to know that not all liquids mix, and as a result there is such a thing as liquid + liquid multicomponent phase diagrams. Examples are shown in Figure 8.11. We will learn to use them by example; for instance, in the case of aniline and hexane shown in Figure 8.11A at point x_1 we have a single liquid phase with a 50% / 50% composition of the two components. Next, upon cooling the solution to point x_2 one observes a liquid-liquid phase separation. Using a tie line at that point reveals that one layer is rich in hexane ($\sim$70%) and the other has more aniline. Surprisingly, it is possible to observe the opposite- liquids that are mixed at a low temperature that separate upon heating. An example included trimethylamine in water. One of the most unusual observations is for nicotine in water as shown in Figure 8.11 B, which has both properties. The components can mix at low and high temperature, but not in between!

8.3.1.4. Liquid-solid and solid-state phase diagrams

Multicomponent phase diagrams may also incorporate the solid state. Shown in Figure 8.12A is the liquid + solid phase diagram of sodium and rubidium. At the high temperature point of x_1 there is a single liquid phase composted of 40% Rb and 60% Na. A solid will precipitate once we cool the liquid to point x_2. Using the tie lines we can read off the diagram that the liquid is composed of 60% Rb and the solid floating in the liquid is made of pure sodium. Upon further cooling to point x_3 we form a solid solution, which is a single mass containing segregated microdomains of sodium and rubidium. Generally one needs a microscope to discern this fact. There is one other interesting feature in this figure, which is the -4.5 $^\circ$C "eutectic point" composed of $\sim$80 % Rb 20 % Na. This represents the lowest temperature at which a liquid can be observed in the phase diagram and is useful for preparing liquid metals at room temperature. This is the principal by which solder works, whereby wires can be bonded to substrates using an alloy of 60% tin / 40% lead that melts at 190 $^\circ$C. This is a relatively low temperature that can be safely applied to electronic circuit boards using a soldering iron.

Phase diagrams can become extremely complex as shown in the solid + solid + liquid example in Figure 8.12B, which is a "reactive" phase diagram between sodium and potassium. The high temperature point x_1 describes a fully liquid system. Solid particles form upon cooling to point x_2 leaving the liquid with a greater percentage of potassium. The solids are not pure metallic sodium, rather Na_2K which is a distinct chemical compound. This is why this phase diagram is labeled as "reactive" as the intermediates found in these systems can have distinct properties. An extreme example can be found in the gallium and arsenic phase diagram, where the two metals combine to form GaAs which is a semiconductor. Concerning sodium and potassium, the compound Na_2K continues to exist even as the liquid component solidifies upon cooling from point x_2 to x_3 where we find a solid

$\sim$94% potassium alloy. This phase diagram also provides an example of “incongruent melting” for the solid compound Na_2K. If we have the pure compound at point x_4 and heat it to the liquid + solid region at point x_5, you don’t get a liquid with the same stoichiometry. Rather it loses its distinct chemical identity as the liquid that forms is a combination of sodium + potassium with a solid that is mostly pure sodium.

Conclusion. In this chapter we have used chemical potential to define the boundaries between phases of state. This was difficult if we attempted to calculate the chemical potentials of all phases over a range of temperatures and pressures, which is why we used the Clausius-Clapeyron equation. This allowed us to define the various phase boundaries so long as we had some data as to the location of the triple point. Multicomponent phase diagrams are, in essence, multiple diagrams that overlap which allows for the determination of the compositions of the various phases as a function of either temperature or pressure. Such representations become complex if the components react to form distinct compounds.

References

1. Goy, C.; Potenza, M. A. C.; Dedera, S.; Tomut, M.; Guillerm, E.; Kalinin, A.; Voss, K. O.; Schottelius, A.; Petridis, N.; Prosvetov, A.; Tejeda, G.; Fernandez, J. M.; Trautmann, C.; Caupin, F.; Glasmacher, U.; Grisenti, R. E. Shrinking of Rapidly Evaporating Water Microdroplets Reveals Their Extreme Supercooling. *Physical Review Letters* 2018, *120*. doi:10.1103/PhysRevLett.120.015501.

2. Kim, K. H.; Spah, A.; Pathak, H.; Perakis, F.; Mariedahl, D.; Amann-Winkel, K.; Sellberg, J. A.; Lee, J. H.; Kim, S.; Park, J.; Nam, K. H.; Katayama, T.; Nilsson, A. Maxima in the Thermodynamic Response and Correlation Functions of Deeply Supercooled Water. *Science* 2017, *358*, 1589-+. doi:10.1126/science.aap8269.

CHAPTER OVERVIEW

9: Surfaces, Interfaces and Electrochemistry

While burning oil is easy, there won't always be oil to burn. It took millions of years for carbon-based fuels to form on our planet. For example, a large portion of the world's coal stock was generated during the Carboniferous period (300M years ago), when the oxygen levels of the Earth were higher. This caused significant plant growth, and bacteria had not yet evolved to the point that they could decompose plant material effectively. All that locked-up energy is now being released over a fraction of the hundreds of million years that it collected, which will have devastating results.

Humanity has long recognized the problem of limited oil resources and has undertaken some lackadaisical effort to add longevity to existing reserves and find alternatives. Catalysts can extend the lifetime of Earth's hydrocarbon feedstock by making chemical transformation more efficient, resulting in less energy consumption. This is usually performed via heterogeneous catalysis using solid-state materials. Examples include the hydrogenation of carbon-carbon double bonds using rhodium nanoparticles, and the Haber-Bosch process that utilizes iron supported on alumina to generate ammonia from H_2 and N_2. Regardless of our ability to extend the lifetime of our oil reserves, they will run out eventually which is why we need to turn to renewables such as wind, water, and solar. Of these, solar is the only sensible choice. Solar energy comes in many forms; for example, the sun can be used to generate fuel. Essentially, the idea is to create carbon-carbon bonds that we subsequently burn like normal, for which we need new and effective solid-state catalysts to make such transformations efficient. Solar energy can also be harnessed using photovoltaics (solar cells). However, we must be able to store the energy generated during the day for use at night, especially at $\sim$6 pm when there is a strong spike in electrical consumption because people are coming home from work. The use of batteries is a good solution, and to understand batteries, we must explore electrochemistry.

All of these processes are inter-related because they involve interfacial phenomena. Heterogeneous catalysts work due to reactions occurring on their surfaces. Likewise, photovoltaics and batteries have metal electrodes where charge transport occurs. For example, in batteries electrons are transferred across a metal rod's surface into (or out of) an electrolyte, and often the electrode is part of the process. We will discuss these examples further on, but for now we will focus on the properties and synthesis of inorganic nanoparticles. These sub-microscopic solids are small to the point that an appreciable number of atoms reside on the surface.

9.1: Surfaces and Surface Energy

We have been ignoring the thermodynamics of surfaces and interfaces throughout this text. Were we were justified in doing so? To evaluate, we will make what is called a “back of the envelope” calculation, which is a rough estimation of the magnitude of a physical quantity via a simple phenomenological model; this exercise is developed in example problem 9.1. The results demonstrate that the number of surface atoms is a very small percentage of the same in the bulk; so we can probably justify our previous dismissal of surface energy. However, if we repeated the calcuation with a 20 nm NaCl particle, then $\sim$13% of the atoms reside on the surface. What are the energetic consequences when a fair number of atoms are on the surface?

Let’s define the internal energy (U) of the nanoparticle. To do so we will split the energy into two contributions, a bulk part plus surface energy which is just like an excess function that we examined in Chapter 7 with solutions. It is easy to calculate the energetic contribution from bulk atoms, we simply divide the per molar energy internal energy (U) by Avogadro’s number (N_A), and then multiply the result by the number of interior atoms (N). Taking a similar approach for the surface energy prompts us to determine the internal energy per unit area and multiply it by the total area of the surface. The total internal energy is thus:

$$U = N \cdot \frac{U_m}{N_A} + A \cdot \gamma \tag{9.1.1}$$

where γ is the internal energy per unit area. Unfortunately, defining γ is problematic. For one, it isn’t clear how to define what constitutes a particle’s surface. To understand, we will use a specific example of a material, zinc sulfide (ZnS), which has an overall cubic unit cell as shown in Figure 9.1. Zinc sulfide’s “zinc blende” structure defined by the location of the zinc and sulfur atoms in the unit cell. The bulk structure is generated by translating the unit cell in a replicative manner (up, down, left, right etc.) as shown in the figure. We can already see that the large crystal has six flat surfaces, or we can create one by cutting through it. This is where understanding surfaces becomes more complex- the cut can be made at various angles, and the surface properties such as the number of atoms per unit surface area depends on how we make the cut. Furthermore, we may be able to make the surface composed of either one type of atom or another depending on where we slice it. We expect different surface energies if the surfaces are made of different atoms! Thus, we need a way to describe the type of surface we are calculating the energy of.

9.0.1 Miller Indices

There exists a system for classifying the type of surface that is being studied. We won’t discuss crystal unit cells further, other than to note that there are many types and shapes of unit cells that are replicated in space to generate the bulk material.

Earlier we discussed how surfaces can be made from cutting a perfect crystal. Shown in Figure 9.2 are some examples, such as a cut across the front face (Fig. 9.2 A). We could also cut through the diagonal or across the center of the crystal (Figs. 9.2 B, C) or cut off a corner (Fig. 9.2 D). All of these surfaces are distinct, and as such we need a method for distinguishing all of them apart. The way to do this was developed by William Hallowes Miller, a Welsh mineralogist, in 1839. Each surface can be described by a plane which bisects the **x**, **y**, and **z** coordinate axes at some point, even if that crossing point is ∞ in the case of the plane being parallel to that axis. Shown at the top of the figures is the point at which the plane bisects the coordinates; the Miller index is simply the inverse of those points.

To demonstrate how surfaces with different Miller indices are different, shown in Figure 9.3 are ZnS $\{100\}$ and $\{111\}$ planes defined as above. Next, we rotated the cube such that the planes are directly facing up, facing you like a mirror in the bathroom. As can be seen, the surfaces appear very different, where the $\{100\}$-type appears as small squares and the $\{111\}$ is composed of small triangles that form interlocking hexagons. Also shown are transmission electron microscope images of a particle with those surfaces pointed up. Again, we see how the appearance is not just something that the model looks like, it is in fact real.

9.1.2. Surface energy

Now that we can discuss specific surfaces, we now must define how they differ energetically. To do so let us consider what is surface energy? Given that we have been discussing preparing surface via cleaving a crystal, one definition is the reversible work necessary to create the surface. Also recall from Chapter 5 that the changes in Helmholtz and Gibbs energies are equal to reversible work. Another way to view surface energy is to realize that surface atoms are missing bonds as shown in Figure 9.4 Here one can see that a, given the structure of the unit cell, that a bulk atom has 4 nearest neighbors and 12 next-nearest neighbors (4 in plane and 8 more “up” and “down”). However, at a $\{100\}$ surface there are 3 nearest neighbor and 8 next-nearest neighbor atoms. Clearly this isn’t “good” for the atom, which means that surface energy is inherently energetically raising. For the $\{111\}$ surface the situation is worse- there are two missing nearest neighbors and 4 missing next-nearest neighboring atoms. Clearly this surface must have even higher energy! In fact, it is a trend that the surface energy correlates with higher Miller indices as can be seen in Table 9.1 for the [GrindEQ__1_A200_A200_] vs. [GrindEQ__1_A201_A201_] surfaces of ZnS and NaCl.

9.1.3 Nanoparticles and surfactants

The nature of surface energy is hopefully clear given that surface atoms are missing bonds and bonding partners. There is an additional, somewhat complicating dynamic that also affects surface energy, which is reconstruction. Surface atoms may “compress” to the nearest neighbors that they have to try to regain electron density. This is especially observable in nanoparticles that have high surface to volume ratios. As shown in Figure 9.5, small nanoparticles of semiconducting CdSe…

9.1.4. Surface tension

Surface energy, \gammaup, is exactly as described above. As for surface tension, \sigmaup, you are already familiar with this because surface tension is why bubbles are round and why you were able to see bugs can walk across the water of a stream.

Material, surface, termination	Surface Energy (\gammaup, J/m^2)
ZnS [GrindEQ__100_], Zn	1.12[a]
ZnS [GrindEQ__100_], S	1.30[a]
ZnS [GrindEQ__111_], Zn	0.87[a]
ZnS [GrindEQ__111_], S	1.01[a]
NaCl [GrindEQ__100_]	0.30
NaCl [GrindEQ__110_]	0.40

Table 9.1 Surface energies and tension for various solids and liquids.

Liquid	\sigmaup, Surface Tension (mN/m)
Water (25 °C)	71.97
Mercury	487

9.2: Surface Expansion Work

This textbook has thus far exclusively examined the thermodynamics of volume-type work, where energy is realized by multiplying volume by its conjugate pressure. Although difficult to conceptualize, work is also performed by expanding a surface: $\partial w = F\partial A$, where A is the area and F is the energy per unit area, otherwise known as surface tension. Already we note that there is a very important difference compared to a gas's pressure-volume work: $\partial w = -P_{ext}\partial V$; basically where is the minus sign? First, let us study the internal energy of a system performing reversible, isothermal pressure-volume work: $\partial U = 0\ J = T\partial S - P\partial V$

which requires $\partial S = \frac{P}{T}\partial V = \frac{nR}{V}\partial V$. When integrated, we find that: $\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$, a familiar equation from Chapter 4. As a result, it is fundamentally true that an increase in volume results in greater entropy. This makes sense when we think of a compression as imparting order; after all, if you compress a gas completely, it may collapse into a perfect crystal with no entropy at all!

Now we ask why the expansion of surface area is positive work. Let's remove the possibility of pressure-volume work and insert in its place the energy for a surface:

$$\partial U = T\partial S + \gamma\partial A$$

assuming a reversible, isothermal surface expansion requires: $\partial U = 0\ J = T\partial S + \gamma\partial\sigma$ and as such:

$$\partial S = -\frac{\gamma}{T}\partial A$$

which integrates to: $\Delta S = -\frac{\gamma}{T}\Delta A$. As a result, increasing surface area results in a decrease in entropy of the system, which at first appears counter-intuitive as one naturally would like to make surface expansion work analogous to volume expansion. To resolve, we need to think about what types of system realistically can experience a surface area change, for which we immediately realize- rubber bands.

Shown in Figure 9.6 is a representation of the interwoven polymer strands that comprise a rubber band, which is a $\sim$2-dimentional material and thus makes a good model for a surface. For the rubber band to be stretched the polymers must be fairly orderly, which is a low entropy state. When compressed the polymer strands are all tangled all over, which clearly indicate that surface entropy is increased when the surface area is extended.

For a theory to be proven true there must be an experiment that validates it. To do so, we got a 4 ft. rubber band and tied the end to a hammer as shown in Figure 9.7 Next, the rubber band was heated over its length with a heat gun. Now, let's predict the outcome-heating will cause disorder as shown in Figure 6.1B. The resulting increase in entropy must be realized by randomization of the elastic band's polymer strands, which will then shorten its overall length. As shown in the figure, the hammer raises by $\sim$1 in. Therefore, heating shortens the rubber band, and while the effect is fairly slight, the shortening of the which is highly counterintuitive.

9.2.1 Surface related phenomenon: pressures of small droplets

We think of work as force times a change of distance, which we saw in Chapter 2 is the same as pressure times a change of volume. Let's apply the same analysis to a droplet. Considering the work to expand a surface, here the curved surface of a sphere, we find that:

$$\partial w = \gamma\partial A$$

where the surface tension γ has units of N/m and $\partial\sigma$ is in m^2. Consider the change in surface area of a sphere with radius r as it grows by ∂r. A sphere has a surface area $4\pi r^2$, and a sphere with a radius $r + \partial r$ has a surface area of:

$$4\pi\left(r + \partial r\right)^2 = 4\pi r^2 + 8\pi r \cdot \partial r + 4\pi(\partial r)^2$$

If we assume that $4\pi(\partial r)^2$ is very small compared to $8\pi r\partial r$ and can thus be ignored, then the change of surface area is:

$$\partial A = 4\pi r^2 + 8\pi r \cdot \partial r - 4\pi r^2 = 8\pi r \cdot \partial r$$

Now when we insert this into the equation for work we find:

$$\partial w = \gamma \partial A = 8\pi\gamma r \cdot \partial r$$

As work is force times a change of distance and ∂r is that change of distance, then $8\pi\gamma r$ is the force that a spherical surface imparts on the interior. Force over area is pressure, and as a result, the surface tension pressurizes the interior of a droplet by:

Pressure = $\frac{Force}{Area} = \frac{8\pi\gamma r}{4\pi r^2} = \frac{2\gamma}{r}$

where again we use the fact that the area of a sphere is $4\pi r^2$.

The pressure inside a sphere must equal the exterior pressure if a droplet is to retain a stable, rounded shape. The exterior pressure includes the above resulting from surface tension in addition to the normal pressure (we assume it is P). As a result, the interior pressure of a droplet is:

$$P_{int} = P + \frac{2\gamma}{r}$$

This means that small droplets have higher interior pressures compared to larger ones.

As it applies to soap bubbles, we have to make a small change to the expression above: $P_{int} = P + \frac{4\gamma}{r}$, because a soap bubble technically has pressure arising from both the interior and exterior of the round soap film. The fact that a smaller bubble is under higher pressure is likely intuitive to you as most of us liked to blow soap bubbles as children. Ever see two fuse together? As shown in Figure 9.8, when that happens you may recall that the smaller one seems to get “sucked into” the bigger bubble. That’s because it’s under higher pressure, thus is collapses when the interior is exposed to the lower pressure inside the larger one which appears to grow.

9.2.2 Phase diagram: The Gibbs–Thomson equation

In the previous section we demonstrated how surface tension causes the interior pressure of a small particle to be higher than the bulk material. This has an important effect when a solid crystal is beginning to form in a freezing liquid. Initially, the particle must have nano-sized dimensions, and thus it will have a higher internal pressure. This in turn increases the chemical potential such that the small solid particle is not thermodynamically stable. Thus, one can ask how do things ever freeze? It turns out that if the temperature is lower than the freezing (fusion) point, then the nucleating solid particles are stabilized.

In this section we study the thermodynamics of nanoparticle stability using the example of solid particle nucleating in a freezing liquid as shown in Figure 9.X. Initially we will assume that the chemical potentials are equal:

$$\mu_{liq} = \mu_{solid}$$

However, we know that the solid nanoparticle has a higher internal pressure (P) compared to the bulk (P°) which raises its chemical potential: \({\mu }_{solid}+\int{}\partial {\mu }_{solid}={\mu }_{solid}+\int^P_{P^*}{}V^{solid}_m\partial P). Thus, the temperature (T) must be lower than the bulk freezing temperature (T_{fus}) to offset this. The chemical potential thus has two corrections, one for pressure and temperature:

$$\mu_{solid} + \int_{T_{fus}}^{T} -S_m^{solid}\partial T + \int_{P^\circ}^{P} V_m^{solid}\partial P$$

where $P>P^\circ$ and $T < T_{fus}$. Concerning the surrounding liquid, it must experience the same decrease in temperature which also affects its chemical potential:

$$\mu_{liq} + int\partial\mu_{liq} = \mu_{liq} + \int_{T_{fus}}^{T} -S_m^{liq}\partial T$$

The temperature (T) can be found where chemical potentials of the solid nucleating nanoparticle and surrounding liquid remain equal:

$$\mu_{liq} + \int_{T_{fus}}^{T} -S_m^{liq}\partial T = \mu_{solid} + \int_{T_{fus}}^{T} -S_m^{solid}\partial T + \int_{P^\circ}^{P} V_m^{solid}\partial P$$

There is no pressure-volume modulation of the liquid’s chemical potential as it is in the bulk state. The solid isn’t so lucky, and its chemical potential is raised by internal pressure as:

$$\int_{P^*}^{P} V_m^{solid}\partial P = V_m^{solid}\cdot\Delta P = V_m^{solid}\cdot\frac{2\gamma}{r}$$

using the relationship $P_{int} = P + \frac{2\gamma}{r}$ from section 9.1.1.

As for the effect of temperature, we combine the temperature integrals on the left side:

$$\mu_{liq} - \mu_{solid} + \int_{T_1}^{T_2} -S_m^{liq}\partial T + \int_{T_{bulk}}^{T} S_m^{solid}\partial T = V_m^{solid}\cdot\frac{2\gamma}{r}$$

and then combine them because they have the same limits:

$$\int_{T_{fus}}^{T} -S_m^{liq}\partial T + \int_{T_{fus}}^{T} S_m^{solid}\partial T = \int_{T_{fus}}^{T}\left(S_m^{solid} - S_m^{liq}\right)\partial T = \int_{T_{fus}}^{T} -\Delta S_{fus,m}\partial T = -\Delta S_{fus,m}\left(T - T_{fus}\right)$$

Since we have already established that: $\mu_{liquid} - \mu_{solid} = 0\ J/mol$ we are left with:

$$-\Delta S_{fus,m}\left(T - T_{fus}\right) = V_m^{solid}\cdot\frac{2\gamma}{r}$$

which can be rearranged as:

$$T = T_{fus} - \frac{V_m^{solid}}{\Delta S_{fus,m}}\cdot\frac{2\gamma}{r}$$

where the entropy change of fusion is defined by the entropy per mole of the liquid state minus the solid state. As in section , we can use the enthalpy of fusion divided by the fusion temperature to represent the change in entropy,$DeltaS_{fus,m} = \frac{\Delta H_{fus,m}}{T_{fus}}$:

$$T = T_{fus} - \frac{T_{fus}\cdot V_m^{solid}}{\Delta H_{fus}}\cdot\frac{2\gamma}{r}$$

The Gibbs-Thomson equation describes some well-known effects, such as the aging of ice cream. It gets crunchier, doesn’t it? That’s because the smaller ice crystals are melting in the freezer if it isn’t cold enough, which makes the bigger ones even bigger. Thus, over time you feel like your biting down on a mouthful of ice cubes! A few other examples are shown in Figure 9.9, such as DSC calorimetry on porous glass soaked in benzene that shows freezing of the liquid in smaller pores occurring at lower temperature than the bulk liquid. Also aluminum metal particles show size-dependent melting points once they are on a nanometer-size scale. Although the temperature drop isn’t very large, you can imagine that engineers need to take these data into account when designing microelectronic components because heat becomes a bigger problem once the circuits themselves become smaller and smaller.

9.2.3 Phase diagram: The Kelvin and Ostwald-Freulich equations

Now let’s move from solid-liquid to liquid-gas equilibrium as a function of size. consider the concept of equal chemical potentials of a vapor originating off a water droplet surface and the interior liquid. In this case:

$$V_m^{liq}\cdot\partial P^{liq} + S_m^{liq}\cdot\partial T = V_m^{vap}\cdot\partial P + S_m^{vap}\cdot\partial T$$

where the changes in pressure of the liquid ∂P^{liq} is not the same as the gas ∂P because of the effect of the addition of pressure due to the surface tension. For the purposes of this demonstration, let us consider the temperature constant, and thus $\partial T = 0\ K$. We are left with:

$$V_m^{liq}\partial P^{liq} = V_m^{vap}\partial P$$

Now consider how the relationship would change as a function of changing radius. Since the liquid phase is in the interior of the droplet:

$$\partial P^{liq} = \partial\left(P + \frac{2\gamma}{r}\right) = \partial P + 2\gamma\cdot\partial\left(\frac{1}{r}\right)$$

Plugging this into $V_m^{liq}\partial P^{liq} = V_m^{vap}\partial P$ from above along with some simplification:$\partial P + 2\gamma\cdot\partial\left(\frac{1}{r}\right) = \frac{V_m^{vap}}{V_m^{liq}}\partial P$

Now we will bring ∂P over to one side and $2\gamma\cdot\partial\left(\frac{1}{r}\right)$ to the other:

$$\partial P-\frac{V_m^{vap}}{V_m^{liq}}\partial P=\left(\frac{V_m^{liq}}{V_m^{liq}}-\frac{V_m^{vap}}{V_m^{liq}}\right)\partial P=-\left(\frac{V_m^{vap}-V_m^{liq}}{V_m^{liq}}\right)\partial P=-2\gamma\cdot\partial\left(\frac{1}{r}\right)$$

Thus:

$$\frac{V_m^{vap}-V_m^{liq}}{V_m^{liq}}\partial P=2\gamma\cdot\partial\left(\frac{1}{r}\right)$$

Now we assume that the volume of the vapor is much higher than the liquid $V_m^{vap}-V_m^{liq}\approx V_m^{vap}$, and we will turn to our old friend the perfect gas law: $V_m^{vap}\approx\frac{RT}{P}$. Thus:

$$2\gamma\cdot\partial\left(\frac{1}{r}\right)=\frac{RT}{V_m^{liq}}\frac{\partial P}{P}$$

Integration of both sides yields:$\int_{0\,m^{-1}}^{\frac{1}{r}}2\gamma\cdot\partial\left(\frac{1}{r}\right)=\int_{P^*}^{P}\frac{RT}{V_m^{liq}}\frac{\partial P^{vap}}{P}$

where P° is the pure partial pressure. The left side is: $\int_{0\,m^{-1}}^{\frac{1}{r}}2\gamma\cdot\partial\left(\frac{1}{r}\right)=2\gamma\cdot\frac{1}{r}$ and the right is: $\frac{RT}{V_m^{liq}}\ln\left(\frac{P}{P^*}\right)$. Equating the two: $\frac{RT}{V_m^{liq}}\ln\left(\frac{P}{P^*}\right)=2\gamma\cdot\frac{1}{r}$ yields the Kelvin equation:

$$\ln\left(\frac{P}{P^*}\right)=\frac{2\gamma V_m^{liq}}{RT}\cdot\frac{1}{r}$$

And thus $P=P^*\cdot exp\left(\frac{2\gamma V_m^{liq}}{RT}\cdot\frac{1}{r}\right)$. As a result, we see that the partial pressure of a vapor originating off a liquid droplet is higher than from a bulk source. Eventually, a droplet can be so small that it has a higher partial pressure than the surrounding atmosphere, whereupon is disintegrates.

There is another interesting aspect of the above relationship which is revealed by a units analysis:

$$\frac{2\gamma V_m^{liq}}{RT}=\frac{J/m^2\cdot m^3/mol}{J/K/mol\cdot K}=meters$$

Furthermore, if one inserts typical values into the above for molar volumes and surface energies as in the example problem, then this lengthscale is one the order of a few nanometers. Consequently, the factor $\frac{2\gamma V_m^{liq}}{RT}$ is often described as a critical radius R_{crit}, which allows us to demonstrate the Ostwald-Freulich equation:

$$P=P^*\cdot e^{\frac{R_{crit}}{r}}$$

Here we can see that if a water droplet is smaller than its critical radius, then its vapor pressure rises dramatically. The droplet is unlikely stable, and will evaporate allowing the water molecules to adhere to the surfaces of larger droplets making them even larger. This process is called Ostwald ripening, a behavior that is observed in many different systems aside from water mist. The example of ice cream becoming crunchier over time is one. Another is in geology, where “phenocrystals” are often observed in rocks. In chemistry, we like to make nanoparticles.

9.2.4 Nanoparticle Synthesis: The Lamer Model

The synthesis of small inorganic nanoparticles, such as the gold colloids that give color to stained glass windows, allows us to summarize all the size-dependent phenomena that has been discussed thusfar. Metal and semiconductor nanoparticles are at the forefront of materials science research due to the increase in surface area which is beneficial for catalysis and the ability to tune many physical properties with size. Such nanoparticles need to be synthesized which is a whole field of science in chemistry. The “burst nucleation theory” of LaMer provides a framework for understanding the thermodynamic basis for many of the existing methods.

As we have discussed, nature abhors a surface because creating surface area decreases entropy (or, equivalently there is a positive changes in Gibb’s energy at constant pressure and temperature). Counter to this is the fact that forming bonds is generally energetically downhill, and scales with volume because more bonds take up more volume. Consequently, we can write a phenomenological model for the Gibbs energy of formation of small particles:

$$\Delta G = 4\pi \cdot \gamma \cdot r^2 - \frac{4}{3}\pi \cdot r^3 \cdot |\Delta_f G_V|$$

where γ is the surface energy and $|\Delta_f G_V|$ is the absolute value of the Gibbs energy of formation per unit volume. The fundamental revelation with the above is that the energy rises as r^2 and decreases as r^3. As a result, for r $<<$ 1 the area term is dominant while the opposite is true when r>>1. Consequently, we see that small particles are not stable but if they can just get big enough they just might keep growing.

If small particles are unstable, then how is it that anyone is able to synthesize nanoparticles to begin with? In the 1950's Victor LaMer developed a standard model to describe how such small using the preparation of colloidal sulfur in a water/acetone solution as shown in Figure 9.10.

9.3: Electrochemistry and the Nernst Equation

Batteries are an integral part of renewables.

Burning gas:

$C_8H_{18}(g) + 25/2\ O_2\ (g) \rightarrow 9\ H_2O(g) + 8CO_2\ (g)$ ΔG=-5,300 kJ/mol octane = 44 MJ/kg octane

Problems: security, sustainability, climate, environment.

Alternative:

$H_2\ (g) + 1/2\ O_2\ (g) \rightarrow H_2O\ (g)$ ΔG= -237 kJ/mol H_2 = 120 MJ/kg H2

Two problems: storage at STP 1L H2 contains 10 kJ of energy

Production: steam reforming

$CH_4\ (g) + H_2O\ (g) \rightarrow CO + H_2\ (g)$ ΔG= -237 kJ/mol H_2 = 120 MJ/kg H2

$CO + H_2O \rightarrow H_2 + CO_2$

H_2 is produced industrially from steam reformation & WG shift reaction:

$CH_4\ (g) + 2H_2O(g) \rightarrow 4H_2\ (g) + CO_2\ (g)$ 9 Mtons/year in US

A viable economy requires an energy consumption rate of $\sim$30 TW in 2050

$\sim$1800 Mtons H2/year

Sun delivers energy at 120,000 TW

9.3.1 Battery Design: The Galvanic Cell. A battery is a type of galvanic cell, which produces electricity based on a spontaneous reaction. The cell is composed of electrodes, which are metallic conductors inserted into a phase boundary across which a potential difference occurs.

Consider the device shown in Figure 9.6, which is a bucket of acid with two metal rods sticking out of it. One is made of zinc and the other copper, and …

9.3.2 The standard electromotive force. These are based on Faraday's Laws:

[GrindEQ__1_] The mass of a given substance that is produced or consumed at an electrode is proportional to the quantity of electrical charge passed through the cell.

[GrindEQ__2_] Equivalent masses of different substances are produced or consumed at an electrode with the passage of a given quantity of electrical charge through the cell.

Gibbs Free Energy: G = H – TS = U + PV – TS

Electrochemical cells operate at constant T and P

Δ��= Δ��+��Δ�� −��Δ��

First law of Thermo: Heat (q) and work (w) are the two forms in which internal energy (U) is transferred to and from a system

Δ��=��+��

And work could be mechanical (pressure-volume, PV) work or electrical work (wel)

Δ��=��+��_����−��Δ��

If the cell is reversible, then qrev = TΔS (2nd law of thermo), and putting it all together:

Δ��=��Δ��+��_(����,������)−��Δ��+��Δ�� −��Δ��=��_(����,������)

Δ��= ��_(����,������)=−����=−������

Cell potentials can be determined away from standard conditions using the Nernst equation:

\[E=E{}^\circ ~-~\frac{RT}{nF}

ParseError: invalid DekiScript (click for details)

\ln \ Q\ \nonumber \]

For any conditions, \(\Delta G=RT

ParseError: invalid DekiScript (click for details)

\ln left(\frac{Q}{K}\right)=~\ -RT

ParseError: invalid DekiScript (click for details)

\ln \ K+RT

ParseError: invalid DekiScript (click for details)

\ln \ Q=~\Delta G{}^\circ +RT

ParseError: invalid DekiScript (click for details)

\ln \ Q)

And, we've established that $\Delta G^{\circ} = \ --nFE^{\circ}$. It follows that away from standard conditions, $\Delta G = -nFE$.

So, \(\Delta G=-nFE=-nFE{}^\circ +RT

ParseError: invalid DekiScript (click for details)

\ln \ Q) and dividing each term by –*nF*,

\[E=E{}^\circ ~-~\frac{RT}{nF}

ParseError: invalid DekiScript (click for details)

\ln \ Θ\ \nonumber \]

Reference electrodes:

Electrical potential (like any potential energy) requires a reference.

Any electrode in which all components of the reaction are present at unit activity has a fixed potential at constant temperature and pressure, and can be used as a reference electrode.

The international standard is the Normal Hydrogen Electrode

$2H^+$ (aq) + $2e^{--}$ $\rightleftharpoons$ H_2 (g), E° = 0 V

Note, this electrode requires working in strong acid (1 M H+) and bubbling in 1 atm explosive H2 gas. Not practical for battery work. But, we use this reference to measure…

Li+(aq) + e– $\rightleftharpoons$ Li(s), E° = –3.04 V vs NHE (0 V vs. Li+/0)

he overall reaction and potential for a Cu^{2+} / Cu^{+} cell given the following:

$Cu^{2+}{}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)}$ 0.340

$Cu^{+}{}_{(aq)} + e^{-} \rightarrow Cu_{(s)}$ 0.522

Make sure you show how to determine the potential by adding ΔG’s.

References

Mohammed J. Meziani. Christopher E. Bunker, Fushen Lu, Heting Li, Wei Wang, Elena A. Guliants, Robert A. Quinn, Ya-Ping Sun. “Formation and Properties of Stabilized Aluminum Nanoparticles” *ACS Appl. Mater. Interfaces* 2009, 13, 703-709.

CHAPTER OVERVIEW

10: The Kinetic Theory of Gas

When studying the world we measure inputs that originate from single molecules. However, our eyes and ears and $\sim$million dollar spectrometers typically signal average over large populations, generally on the order of a mole (6.022×10^{23}). We would like to understand how to unpack a measurement on a large population to discern the nature of the single species. To do so, we have to learn how to average the properties of molecules using the mathematics of probability. In this chapter we will focus on determining the average translational velocity of a perfect gas. Mostly because it’s tractable, and you can do some neat things like derive the Equipartition theorem from Chapter 2. You will also make an interesting observation about the speed of sound and how the observer’s relation to a system can alter measurements of the same.

10.1: Probability vs. Probability Distribution

You understand probability- what is the likelihood of heads vs. tails in a coin flip? It's 50%, and I'm quite sure that even my drooling cat knows this! Let's go a step further- what is the probability of getting two heads when flipping two coins at once? To evaluate, divide the number of results you are interested in by the total number of possible outcomes:

Outcome 1	heads	heads
Outcome 2	heads	tails
Outcome 3	tails	heads
Outcome 4	tails	tails

We see four potential outcomes, and only one of them is the result we are interested in. Thus, the probably of heads-heads is ¼ = 0.25 = 25%. Note that this is the same as the product of the probability of heads on two sequential coin flips: 0.25 = 0.5 × 0.5. Likewise, the probability of observing an even 50/50 split for a 2 coin toss, i.e either heads-tails or tails-heads, is 50%.

Now imagine that you're studying a gas in an enclosed chamber, the purpose of which is to understand the nature of the individual molecules. You are allowed to make one observation using a spectrometer that informs how many molecules are displaying the "heads" property. Since we suspect that the gas is composed of even-sided "coin" molecules we believe that exactly half the molecules should be "heads". The following table the odds that you will observe a 50/50 split, called P(50/50). And while we established that the P(50/50) odds are 50% for two gas molecules, your intuition likely tells you that the probability for an exact even split drops as the population increases. This is in fact the case:

# coins	P(50/50)
2	50%
4	37.5%
100	7.96%
1000	2.52%
10,000	0.80%
100,000	0.255%
N_A	$\sim$0%

Based on the limiting behavior we can conclude that the probability of a perfect even split is 0% if observing an entire mole of "coin" molecules. We have come to the conclusion that the individual species ***do not*** have even sides, which is totally wrong!

The lesson here is that probability probably isn't helpful when simultaneously examining large populations of single molecules. The solution is to add some "wiggle room". For example, for 100 molecules there is only an $\sim$8% chance of observing exactly 50 heads and 50 tails. However, the odds of observing 50 ± 3 heads, i.e. between 47 → 53, are $\sim$52%. Likewise, if we ping 1000 molecules the probability is $\sim$51% for observing 500 ± 10 heads. Consequently, consideration of a spread in the results returns the correct microscopic description of an even-sided "coin" molecule. Let's add this information to the table:

# Molecules	P(50/50)	±Spread (%)	P(50/50 ± Spread)
100	7.96%	3 (6.0%)	51.7%
1000	2.52%	10 (2.0%)	51.3%
10,000	0.80%	30 (0.60%)	50.2%
100,000	0.255%	105 (0.21%)	50.01%

Table 10.2. Incorporating a spread of potential observables yields higher probabilities.

We need a new mathematical expression for the probability that incorporates a spread. To do so, let's state that we are investigating property y and we wish to know the probability of observing it. Since y is observed over a very large population, we have to incorporate a spread in y just like in the above example. Mathematically we use the expression: $P = P_{dens}(y) \cdot \Delta y$ to redefine the probability. Here, P is the probability we are familiar with, Δy is the spread, and $P_{dens}(y)$ is a function that is like (but not exactly) a probability. We will call it the probability density, and we plot it in Figure 10.1 for the example of 10,000 "coin" molecules. Essentially it is a normalized histogram of the number of heads observed from a very, very large number of measurements. Also, "normalized" means that the area under the curve is 1.0. The curve is bell-shaped (also called "Gaussian") and is centered at 5,000 heads, which makes sense for 10,000 even-sided "coin" molecules. The fact that the area under the curve 1.0 means that there is a 100% chance that, when a measurement is made on a population of 10,000, the number of heads measured will be somewhere between 0 and 10,000. Of course that's true! The area from 49,970 to 50,030 is 0.502 = 50.2%, which means that if we ask the probability of measuring 5,000 $\pm$ 30 heads the answer is $\sim$50%. Thus, when we ask the right questions, we regain the ability to discern the fact that the coin molecules have two even sides!

When we examine Table 10.2 further we see that the %spread drops as the population increases (fyi: the spread of 6% for 100 coins is calculated as $\frac{3}{50} = 6\%$). This is akin to stating $\Delta y \to \partial y$, which makes our expression for probability:

$$P = P_{dens}(y) \cdot \Delta y \to P_{dens}(y) \cdot \partial y$$

We have discussed the properties of partials in previous chapters but we will review them here. First, a partial has units, and a probability has no units (it's like a fraction or a percentage). Consequently, we see that the probability density $P_{dens}(y)$ has inverse units of the property y that is under investigation. Second, a partial is technically infinitely small, so the value of ∂y is 0. To understand the impact of this, let's switch from the game of heads and tails to study something more important, such as the probability that a gas phase molecule has a very specific kinetic energy E_i. The probability that a molecule has exactly E_i of kinetic energy is: $P(E_i) = P_{dens}(E_i) \cdot \partial E = 0\ \%$, which is not very useful. However, when we see a partial we know that it must be integrated to have any value. When we do so we can start making observations as to the nature of probability densities such as the following: $\int_{0\,J}^{\infty\,J} P_{dens}(E) \cdot \partial E = 1.0$. This is the property of normalization, which means that the probability of having some energy (or no energy at all) is 100%. In fact, all probability densities have to be normalized such that the following is always true when integrated over all possible values:

$$\int_{lower\,limit}^{upper\,limit} P_{dens}(y) \cdot \partial y = 1.0$$

10.1.1 Averages. Probabilities are calculated from integrating probability densities. There are some interesting tricks you can do with this, such as calculate the probability that a molecule is simultaneously moving up and sideways etc.; you can work some examples in problem set questions. What is more useful is calculating the average value of a property such as energy: $<E>$. Probability distribution are both useful and often necessary for determining as much, and the correct calculus expression is: $<E> = \int_{0\,J}^{\infty\,J} E \cdot P_{dens}(E) \cdot \partial E$ where you integrate the thing you want the average of times its probability distribution over all possible values. In general, for any property y:

$$\langle y \rangle = \int_{lower\,limit}^{upper\,limit} y \cdot P_{dens}(y) \cdot \partial y$$

What is more interesting is that you can also determine what are called higher "moments", such as the 2^{nd} moment (the average of the square) of property y:

$$\langle y^2 \rangle = \int_{lower\,limit}^{upper\,limit} y^2 \cdot P_{dens}(y) \cdot \partial y$$

You can even calculate averages using stipulations. For example, the velocity of a molecule in any direction can be between –∞ m/s and ∞ m/s since it can go backwards. Thus, you can calculate things like the average velocity in the positive x-direction only by adjusting the limits of integration as so:

$$\langle v_x \rangle_+ = \int_{0\,m/s}^{\infty\,m/s} v_x \cdot P_{dens}(v_x) \cdot \partial v_x$$

where the "+" subscript means the average is conditional that the molecule is moving forwards.

Shown in Figure 10.2 are several graphs of common probability densities. One is the even “tophat” that describes coin tosses and the chances of winning a lottery- basically a very large number of games of chance. Also shown is the Gaussian, where the average $< y >$ is clearly at the top of the distribution. For a bell-shaped curve the average is coincident with the most probable y, which is labeled y_{mp}. Most probable values are defined to be at the top of the probability distribution, and can be found by solving the expression:

$$\frac{\partial P_{dens}\left(y_{mp}\right)}{\partial y}=0$$

for y_{mp}.This is the calculus expression for the maximum value of a function, i.e. the point where the curve is flat at the maximum. Last, we also see that the root-mean-square average value $\sqrt{\langle y^2\rangle}$ is near the top but to a slightly higher than the average. In fact it is generally true that \(\sqrt{\langle y^2\rangle }) is greater than $\langle y\rangle$.

10.2: The Boltzmann Distribution

Nature has a formula for the probability density of energy, which represents how nature doles out energy to molecules. Unfortunately, the derivation is difficult, so we will instead just discuss the logic of the Boltzmann Distribution . Let's think back to the flip of a coin, where we ask about the occurrence we are investigating divided by all possible results. When applied to energy we might believe that the probability of having energy E_i is: $\frac{E_i}{\sum_i E_i}$. While sensible, this actually doesn't work because this expression would not conserve mass and energy. Instead, Boltzmann figured out that nature uses a similar expression but with exponentials: \(\frac{e^

ParseError: EOF expected (click for details)

{\sum_i{}e^{-E_i}}\). However, there is one last problem which is that the argument of an exponential cannot have units. The answer is to divide E_i by k_BT, which gives us the proper expression for Boltzmann's formula:

\[P_{dens}\left(E_i\right)=\frac{e^{\frac

ParseError: EOF expected (click for details)

}{\sum_i{}e^{\frac{-E_i}{k_BT}}} \nonumber \]

Recall that the Boltzmann constant k_B is simply the S.I. gas constant R = 8.314 J/K/mol divided by Avogadro's number: $k_B = \frac{R}{N_A} = 1.38 \times 10^{-23}\ J/K$. It's like the gas constant for a single molecule.

Now this expression is like a gas engine- powerful, but towards what purpose do we apply it? For our purposes here we will apply it towards calculating the velocities of gas molecules. In the process we will be able to demonstrate some interesting facts about gases, as well as derive the Equipartition Theorem all the way back from Chapter 2. Regardless, as it applies to velocity we will use kinetic energy, i.e. $E_i = \frac{1}{2}mv^2$. Therefore:

$$P_{dens}\left(v\right) = \frac{e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}}{\sum e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}}$$

A clever thing about the above is that we transformed the probability density for energy into the same for velocity simply by inserting the correct expression for energy as a function of velocity.

In the present form the probability density is too difficult to do anything with, so we will simplify it piece-by-piece. We will start with the denominator, which is the part of the expression that normalizes the probability density. First, we have to apply the fact that the Universe is three-dimensional which means $v^2 = v_x^2 + v_y^2 + v_z^2$. The identity $e^{a+b+c} = e^a \cdot e^b \cdot e^c$ helps us show that:

$$\sum e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} = \sum_{v_x=-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}} \cdot \sum_{v_y=-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}} \cdot \sum_{v_z=-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}$$

The summation is performed over negative to positive velocities, which is because gas molecules can move either forward (positive velocity) or backward (negative velocity). This is different that the net velocity: $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$, which cannot be negative. But what's with the sum in the denominator? How do you sum over a variable like velocity that is continuous? The answer is you can't, so we have to replace the summation with an integral. This can be done with an identity called a Riemann sum: $\sum_1^n f\left(x\right) cdot \left(\frac{b-a}{n}\right) = \int_a^b f\left(x\right)\cdot\partial x$. Based on this identity it's important that we have a factor like $\left(\frac{b-a}{n}\right)$ in our sum, which is the origin for ∂x for the integral. When we examine a denominator term such as: $\sum_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}$, it appears there is no such factor. And as usual, there is a clever answer, which is to multiply and divide the denominator by ∂v_x (and ∂v_y and ∂v_z) which then allows us to transform the triple sum into a triple integral (bold for emphasis):

$$\frac{e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}}{\sum_{v_x=-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\sum_{v_y=-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\sum_{v_z=-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}}=\frac{e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\partial v_y\cdot\partial v_z}{\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\cdot\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z}$$

First we will solve the denominator:

$$\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z\right)$$

While this looks absolutely horrible, in reality there is just one calculus expression because there is no reason why the integral along x will be different that y or z. As a result, we can just solve $\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x$ and then cube the result. We can look up a standard Gaussian-type integral:

$$int_{-\infty}^{\infty} e^{-a\cdot x^2}\cdot\partial x=\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

To apply it to our expression we see: $a=\frac{m}{2\cdot k_B\cdot T}$, which makes the solution to the v_x integral:

$$\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x=\left(\frac{\pi}{\frac{m}{2\cdot k_B\cdot T}}\right)^{\frac{1}{2}}=\left(\frac{2\pi\cdot k_B\cdot T}{m}\right)^{\frac{1}{2}}$$

And the triple integral can be evaluated: $\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z\right)=\left(\frac{2\pi\cdot k_B\cdot T}{m}\right)^{\frac{3}{2}}$

This leaves the Boltzmann probability density in the form:

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\partial v_y\cdot\partial v_z$$

There is one last problem- the argument of the exponential has net velocity squared (v^2) but the partials are directional vectors. Can we just substitute ∂v for $\partial v_x\cdot\partial v_y\cdot\partial v_z$ and hope that is ok? The answer is **no**.

10.1.1 Transformation of Variables. How do we legitimately make the substitution: $\partial v_x\cdot\partial v_y\cdot\partial v_z\rightarrow\partial v$? The first thing to note is that since we start with an expression with a set of three partials, each in an orthogonal dimension (x, y and z), then we must transform into another set of three orthogonal partials. This is a stipulation in information science- you can't just substitute something in 3D ($\partial v_x\cdot\partial v_y\cdot\partial v_z$) for 1D (∂v). If you do so information is lost and any subsequent analyses will be wrong. A simple answer is that we can transform the standard Cartesian velocity coordinates v_x, v_y, and v_z into spherical coordinates v, ϕ, and θ, where the net velocity is just like the radius of a sphere. Such a transformation also replaces the partials. Next, we can integrate ϕ and θ out of existence leaving the probability density with only the partial of net velocity ∂v left. This uses the mathematics of "Jacobians", and is shown for you in the Appendix.

Rather than take a brute force mathematical derivation, here we demonstrate a visual approach to the transformation of Cartesian to spherical coordinates as it applies to partials. First, let's look more closely at integrals and discuss the job of a partial. As shown in Figure 10.3A, a partial moves along the independent (x) direction from the lower limit to upper limit. As it does so, an area is created from the product of the partial's length and the function's height: $f(x)\cdot\partial x$. The integral is the sum of these areas. For a 2-dimensional integral, the two partials ($\partial x\cdot\partial y$) generate an area in the x-y plane as shown in Figure 10.3B. That area is multiplied by the function's height to create volume, and the integral is the sum of these volumes.

Unfortunately, we cannot graph a 3-dimensional partial with a corresponding function, so instead we just draw the partials as shown in Figure 10.4A. Clearly the product of three partials creates a volume element. As we add up more volume elements (up, down, left, right, forward and backwards) we see that essentially the partials grow like a sphere. The solution has now presented itself- as the radius of a sphere grows by ∂r, the increase in volume is that of a shell which is the sphere's surface area ($4\pi\cdot r^2$) times ∂r. When we use the notation appropriate to velocities, the transformation is:

$$\partial v_x\cdot\partial v_y\cdot\partial v_z\rightarrow 4\pi\cdot v^2\cdot\partial v$$

as the net velocity is the same as the radius. Applied to the probability distribution:

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\partial v_y\cdot\partial v_z$$

we now have the Maxwell-Boltzmann equation:

$$4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

The distribution is plotted in Figure 10.5A for O_2 gas as a function of temperature and in 10.5B for He, O_2, and XeF_6 gases at room temperature. The most important feature is that the curve is *almost* bell-shaped, but now quite due to the v^2 skew. The effect of this is to drag the distribution to higher speeds. It is also interesting to see that O_2 can easily reach velocities far in exceed the speed of sound (343 m/s), a very counter-intuitive observation. Heating widens the distribution, but the most significant change occurs with mass. Light elements such as helium have shockingly high velocities; in fact a significant portion of He gas can move faster than escape velocity 11,200 m/s. Does this explain why the Earth is losing helium? Yes, it does, the gas is escaping into outer space. Last, the skew causes the most probable and average velocities to no longer coincide; to demonstrate let’s derive them.

10.3: Average and RMS Velocities

Now that we have the Maxwell-Boltzmann distribution as a function of net velocity we can calculate the average and second moment. The average velocity <v> is determined via:

$$\langle v\rangle = \int_0^\infty 4\pi\cdot v^2\cdot v\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

To simplify matters, we will call all the constants “Q” = $4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}}$, leaving us to solve a less-scary expression: $Q\cdot\int_0^\infty v^3\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$. We can do this using an integral identity as shown in the Example box. However, to improve our math skills we will solve it here the long way using integration by parts:

$$\int_a^b f(x)\cdot\frac{\partial g(x)}{\partial x}\cdot\partial x = f(x)\cdot g(x)]_a^b - \int_a^b\frac{\partial f(x)}{\partial x}\cdot g(x)\cdot\partial x$$

We have to conform the formula above to the Maxwell-Boltzmann distribution. First, we define $f(x)$, whereby $x=v$, a = 0 m/s and b = ∞ m/s. It is tempting to make $f(v)=v^3$, however, the “trick” is to leave one velocity term out which means $f(v)=v^2$ and $\frac{\partial f(v)}{\partial v}=2\cdot v$ The remaining terms define $\frac{\partial g(v)}{\partial v}=v\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$, and thus $g(v)=\left(\frac{-k_B\cdot T}{m}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}$. As a result, the integration by parts gives an average velocity of:

$$\langle v\rangle = Q\cdot f(v)\cdot g(v)]_0^\infty - Q\cdot\int_0^\infty\frac{\partial f(v)}{\partial v}\cdot g(v)\cdot\partial v$$

The first term:

$$Q\cdot f(v)\cdot g(v)]_0^\infty = Q\cdot v^2\cdot\left(\frac{-k_B\cdot T}{m}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\Big|_0^\infty = 0$$

since the limits are evaluated as: $\infty^2 e^{-\infty}\to 0$ and: $0^2 e^{-0}\to 0$.

The second term is:

$$-Q\cdot\int_0^\infty\frac{\partial f(v)}{\partial v}\cdot g(v)\cdot\partial v = 2\cdot Q\cdot\frac{k_B\cdot T}{m}\int_0^\infty v\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

Oddly, we have already evaluated the above because it is basically the same as $\frac{\partial g(v)}{\partial v}$, the integration of which is g(v). Thus:

$$2\cdot Q\cdot\frac{k_B\cdot T}{m}\int_0^\infty v\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v = 2\cdot Q\cdot\left(\frac{k_B\cdot T}{m}\right)\cdot\left(\frac{-k_B\cdot T}{m}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\Big|_0^\infty = -2\cdot Q\cdot\left(\frac{k_B\cdot T}{m}\right)^2\cdot\left(e^{-\infty}-e^0\right)$$

$$= 2\cdot Q\cdot\left(\frac{k_B\cdot T}{m}\right)^2$$

Work through the constants (Q is defined above) to simplify them and you see:

$$\langle v\rangle = \int_0^\infty v\cdot 4\cdot\pi\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot v^2\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v = \left(\frac{8\cdot k_B\cdot T}{\pi\cdot m}\right)^{\frac{1}{2}}$$

10.2.1 Average square velocity. Let’s work out the second moment, i.e. the average squared velocity of a gas $\langle v^2\rangle$, by integration of the Maxwell-Boltzmann distribution. The second moment of velocity is found via:

$$\langle v^2\rangle = \int_0^\infty 4\pi\cdot v^2\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

Again we will remove all the constants by calling them Q = $4\cdot\pi\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}$ and we will us integration by parts to solve $Q\cdot\int_0^\infty v^4\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\partial v$. Like before we use the “trick” of partitioning an odd factor of velocity for: $f(v)=v^3$, which makes

$\frac{\partial f(v)}{\partial v} = 3 \cdot v^2$. This leaves a factor of velocity for: $\frac{\partial g(v)}{\partial v} = v \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v$, the integration of which gives: $g(v) = \left(\frac{-k_B\cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}$.

Now the integration by parts fomula is:

$$\langle v^2\rangle = Q \cdot f(v) \cdot g(v)]_0^\infty - Q \cdot \int_0^\infty \frac{\partial f(v)}{\partial v} \cdot g(v) \cdot \partial v$$

The first term is:

$$Q \cdot f(v) \cdot g(v) = Q \cdot v^3 \cdot \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \Big|_0^\infty = 0$$

since $\infty^3 e^{-\infty} \to 0$ and $0^3 e^{-0} \to 0$. The second term is:

$$-Q \cdot \int_0^\infty \frac{\partial f(v)}{\partial v} \cdot g(v) \cdot \partial v = -Q \cdot \int_0^\infty 3 \cdot v^2 \cdot \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v =$$

$$Q \cdot \int_0^\infty 3 \cdot v^2 \cdot \left(\frac{k_B \cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v$$

which means we must do another integration by parts. We will define g(v) and $\frac{\partial g(v)}{\partial v}$ as above and now: $f(v) = v$ and $\frac{\partial f(v)}{\partial v} = 1$. Next, we factor out the constants:

$$3 \cdot Q \cdot \frac{k_B \cdot T}{m} \cdot \int_0^\infty v \cdot v \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v$$

$$= 3 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right) \cdot v \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \Big|_0^\infty - 3 \cdot Q \cdot \frac{k_B \cdot T}{m} \cdot \int_0^\infty \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v$$

The first term is 0 like in the other examples. The second term is solved using a standard Gaussian integral similar to the one that was introduced earlier: $\int_0^\infty e^{-a\cdot v^2} \cdot \partial v = \frac{1}{2}\sqrt{\frac{\pi}{a}}$. This allows us to demonstrate:

$$\langle v^2\rangle = \int_0^\infty v^2 \cdot 4 \cdot \pi \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \cdot v^2 \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v = 3 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right)^2 \cdot \frac{1}{2} \cdot \left(\frac{2 \cdot \pi \cdot k_B \cdot T}{m}\right)^{\frac{1}{2}}$$

Work through it (remember Q is defined above) and you find:

$$\langle v^2\rangle = \frac{3 \cdot k_B \cdot T}{m}$$

Often we express the above as the root-mean-squre, or rms velocity $\sqrt{\langle v^2\rangle} = \sqrt{\frac{3\cdot k_B\cdot T}{m}}$. This is because it has the same units as average velocity and is thus comparable.

10.2.2 Pressure-volume and the perfect gas equation. We hope that it is interesting that humanity has evolved to the point where we can derive such knowledge of nature without resorting to actually making measurements, which is the end goal of Physical Chemistry. There are a few interesting points that can be made with the derivations thus far. For example, we remind you that the Boltzmann constant is related to the gas constant R via Avogadro's number. As a result, algebraic manipulation of the average square velocity reveals:

$$langlev^2\rangle = \frac{3 \cdot k_B \cdot T}{m} \cdot \frac{N_A}{N_A} = \frac{3 \cdot R \cdot T}{M}$$

where M is the mass in kg per mole. Since all these derivations were performed on a perfect gas, we know that for 1 mole: $P \cdot V = R \cdot T$ and as a result:

$$P = \frac{M \cdot \langle v^2\rangle}{V \cdot 3}$$

Now we can make a simple measurement of the pressure of a gas and know how fast the individual molecules are moving. Score!

10.2.3 Most probable velocity. Here we locate the top of the Maxwell-Boltzmann distribution by first determining the derivative: $\frac{\partial\left(4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\right)}{\partial v}=$

$$8\pi\cdot v\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}+4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot\left(\frac{-m\cdot v}{k_B\cdot T}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}$$

The two terms can be set across the equal sign once we set the expression to 0 s/m, and the velocity terms in the derivative become the most probable because there is only one velocity that maximizes the distribution:

$$8\pi\cdot v_{mp}\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v_{mp}^2}{2\cdot k_B\cdot T}}=4\pi\cdot v_{mp}^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{3}{2}}\cdot\left(\frac{m\cdot v_{mp}}{k_B\cdot T}\right)\cdot e^{\frac{-m\cdot v_{mp}^2}{2\cdot k_B\cdot T}}$$

Several simplifications can me made: $2=v_{mp}\cdot\left(\frac{m\cdot v_{mp}}{k_B\cdot T}\right)$ from which we solve:

$$v_{mp}=\sqrt{\frac{2\cdot k_B\cdot T}{m}}$$

10.2.4 Flux. One of the more interesting things that Maxwell-Boltzmann calculations can be used for is to model the flux of molecules hitting a surface. A flux is the collision rate of gas molecule striking an area per unit time. We express the flux as per unit area so that the data can be applied to different systems. To determine the flux we will use a phenomenological model shown in Figure 10.6. Here we see that a gas molecule is moving to the right, and in Δt time it will strike the wall of area A. It has to travel some distance to do so; this distance is specifically the molecule's speed in the "right-moving" direction times the time (Δt) it takes to reach the wall. We can easily calculate the average speed in the x- (or y- or z-) direction by solving: $\langle v_x\rangle=\int_{-\infty}^{\infty}v_x\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{1}{2}}\cdot e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x$, but hopefully you realize that this is 0 m/s. It also isn't what is being asked- we want to know the average speed of a molecule under the condition that it is only moving to the right, or in other words with a positive velocity. This is:

$$\langle v_x\rangle^+=\int_0^{\infty}v_x\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{1}{2}}\cdot e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x$$

(see the change in the lower limit?) This is solved with the identity$int_0^{\infty}x\cdot e^{-a\cdot x^2}\cdot\partial x=\frac{1}{2a}$:

$$\langle v_x\rangle^+=\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{1}{2}}\cdot\frac{1}{2a}=\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{\frac{1}{2}}\cdot\frac{2\cdot k_B\cdot T}{2m}=\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}$$

Now that we have the length that the red gas molecule is travelling to hit the wall, we now have the volume that the molecule resides in: $\Delta t\cdot\langle v_x\rangle^+\cdot A$. If we simply multiply this volume by the number density (number of molecules per volume in the container), we just calculated how many molecules are going to strike the wall in time Δt. The number density is $\frac{N}{V}$, and thus:

$$\#collisions=A\cdot\Delta t\cdot\langle v_x\rangle^+\cdot\frac{N}{V}=A\cdot\Delta t\cdot\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}\cdot\frac{N}{V}$$

Last, recall that the flux is the number of collisions per unit area per unit time. Consequently:

$$Flux=\frac{A\cdot\Delta t\cdot\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}\cdot\frac{N}{V}}{A\cdot\Delta t}=\left(\frac{k_B\cdot T}{2\pi\cdot m}\right)^{\frac{1}{2}}\cdot\frac{N}{V}$$

Using the perfect gas law \(PV=nRT)can be expressed using the number of molecules N with Avogadro's number: $PV=\frac{N}{N_A}RT$, and since $\frac{R}{N_A}=k_B$ we have:$fracPk_B\cdot T=\frac{N}{V}$. When we use this in the expression above we determine that:

\[Flux={\left(\frac{k_B\cdot T}{2\pi \cdot m}\right)}^{\frac{1}{2}}\cdot \frac{P}{k_B\cdot T}=\frac{P}{\sqrt

ParseError: EOF expected (click for details)

\nonumber \]

Again, we demonstrate how simple measurements like pressure yield information about the individual molecules themselves when you understand their statistical behavior.

10.4: Average relative velocity and collision frequency

Another interesting use of the Maxwell-Boltzmann distribution is to examine how gas molecules interact with each other, and to do so we have to consider our observational frame of reference. By this we mean that, in all the derivations above, we are outsiders looking into a vacuum chamber containing a moderate pressure of gas. However, our observations may change if we are strapped to be back of a gas molecule and riding it around in the same chamber.

How do we observe other molecules if we are one of them? In other words, we go from the laboratory to the molecular frame. To do so, the transformation is that all the velocities are now relative to our own. Let's say we are molecule "a" moving at speed v_a and we see molecule "b" with speed v_b. If "b" is going in same direction at the same speed, it appears not be moving at all. If heading straight towards us, "b" appears to be scarily moving fast. Mathematically we are observing not the absolute velocity but the relative velocity:

$$V_{rel} = v_a - v_b$$

Perhaps we can now perform Maxwell-Boltzmann calculations on relative velocity? Not quite, which is because originally we had a 2-dimensional system of two "a" and "b" velocity vectors. As a result, we still have to perform a 2-dimensional calculation, or we have arbitrarily lost information and our analyses will be wrong (recall this was a problem we encountered when transforming $\partial v_x \cdot \partial v_y \cdot \partial v_z \rightarrow \partial v$).Therefore we define the second orthogonal velocity to V_{rel}, which is the center of mass velocity G shown in the figure above:

$$G = \frac{m_a v_a + m_b v_b}{m_a + m_b}$$

To proceed, we need to be able to write the vectors v_a and v_b in terms of G and V_{rel}. Its just an exercise in algebra and the results are:

$$v_a = G + \frac{m_b}{m_a + m_b} V_{rel}$$

$$v_b = G - \frac{m_a}{m_a + m_b} V_{rel}$$

What do we do with their Maxwell-Boltzmann distributions such that the velocities or "a" and "b" are analyzed together? Let's rather start with this question- what is the probability that "a" is moving forward? Why, its 0.5 or 50%! What about "b"? The same, 50%. Now what is the likelihood that both "a" and "b" are moving forwards? Clearly that's 0.25 = 25%, which is the product of the individual probabilities (like heads-heads in a coin flip).

Now we can answer the question- how do we analyze the velocity distributions for two particles simultaneously? We simply use the product of the individual Maxwell-Boltzmann distributions:

$$MB(v_a) \cdot MB(v_b) = \left(\frac{1}{2\pi k_B T}\right)^3 \cdot (m_a m_b)^{\frac{3}{2}} \cdot e^{-\frac{m_b v_b{}^2 + m_a v_a{}^2}{2k_B T}}$$

The above is just the standard velocity probability distribution using two different masses (m_a and m_b) as well as velocities (v_a and v_b). Notice that the usual Maxwell-Boltzmann factor: $\left(\frac{1}{2\pi k_B T}\right)^{\frac{3}{2}}$ is squared in the equation above. However, the masses are not because the mass for particle "a" and "b" may be different.

Moving forward, the clever thing is to redefine: $m_b v_a^2 + m_a v_a^2$ that appears in the exponential in terms of V$_{rel}$ and G. We expressed v_a and v_b above, and now we square them and do some algebra. There is a cross term $\mathbf{G{\cdot}V}_{\boldsymbol{rel}}$ that has been made bold for emphasis:

$$m_b v_b^2 + m_a v_a^2$$

$$= m_b \left[G^2 + \frac{m_a^2}{(m_a + m_b)^2} V_{rel}^2 - \frac{2m_a}{m_a + m_b} G \cdot V_{rel}\right] + m_a \left[G^2 + \frac{m_b^2}{(m_a + m_b)^2} V_{rel}^2 + \frac{2m_b}{m_a + m_b} G \cdot V_{rel}\right]$$

$$= (m_a + m_b) G^2 + \left[\frac{m_b \cdot m_a^2 + m_a \cdot m_b^2}{(m_a + m_b)^2}\right] V_{rel}^2$$

$$=\left(m_a+m_b\right)G^2+\frac{m_a\cdot m_b}{\left(m_a+m_b\right)}V_{rel}^2$$

Notice how above that the **G·V$_{rel}$** cross terms in the second step cancel? This simplifies the remaining derivation because we can now separate the G and V$_{rel}$. as shown here:

\[MB\left(G\right)\cdot MB\left(V_{rel}\right)={\left(\frac

ParseError: invalid DekiScript (click for details)

{2\pi k_BT}\right)}^3

ParseError: invalid DekiScript (click for details)

ParseError: invalid DekiScript (click for details)

\nonumber \]

Now we are almost ready to integrate the expression, but just like last time we have to be careful with partials. As we started with the expression $MB(v_a)\cdot MB(v_b)$, of course it uses partials of $\partial v_a\cdot\partial v_b$. When transforming: $\partial v_a\cdot\partial v_b\rightarrow\partial G\cdot\partial V_{rel}$, the geometry factor (also known as the "Jacobian") is 1.0; see the Appendix. This means:

$$MB\left(v_a\right)\cdot MB\left(v_b\right)\cdot\partial v_a\cdot\partial v_b=MB\left(G\right)\cdot MB\left(V_{rel}\right)\cdot\partial G\cdot\partial V_{rel}$$

However, we still need to remember that we live in three dimensions. Consequently the expression is:

\[{\left(\frac

ParseError: invalid DekiScript (click for details)

{2\pi k_BT}\right)}^3{e^-}^{\frac{(m_a+m_b)({G_x}^2+{G_y}^2+{G_z}^2)}{2k_BT}}{e^-}^{\frac{\frac{m_am_b}{m_a+m_b}V^2_{rel}}{2k_BT}}\partial V_{rel,x}\partial V_{rel,y}\partial V_{rel,z}\partial G_x\partial G_y\partial G_z \nonumber \]

Ultimately, we want $\langle V_{rel}\rangle$, so we want to remove all the reduced mass velocities (the G's). To do so we integrate them out from $-\infty<G_{x,y,z}<\infty$:

\[\int^{\infty }_{-\infty }{}\int^{\infty }_{-\infty }{}\int^{\infty }_{-\infty }{}{\left(\frac

ParseError: invalid DekiScript (click for details)

{2\pi k_BT}\right)}^3{e^-}^{\frac{(m_a+m_b)({G_x}^2+{G_y}^2+{G_z}^2)}{2k_BT}}\partial G_x\partial G_y\partial G_z={\left(\frac{\left(m_am_b\right)}{2\pi k_BT(m_a+m_b)}\right)}^{\frac{3}{2}} \nonumber \]

This was solved using a standard Gaussian integral; it's actually nearly identical to our derivation of the normalization factor in the velocity Maxwell-Boltzmann distribution. The remaining part of the distribution is only in terms of the relative velocities:

$$\left(\frac{(m_am_b)}{2\pi k_BT(m_a+m_b)}\right)^{\frac{3}{2}}e^{-\frac{(m_am_b)V_{rel}^2}{2k_BT(m_a+m_b)}}\cdot\partial V_{rel,x}\partial V_{rel,y}\partial V_{rel,z}$$

From here, you transform $\partial V_{rel,x}\partial V_{rel,y}\partial V_{rel,z}\rightarrow 4\pi\cdot V_{rel}^2\cdot\partial V_{rel}$ as before and we will also substitute in "μ", called the reduced mass, for $\frac{(m_am_b)}{(m_a+m_b)}$. We can work the average relative velocity expression:

\[\langle V_{rel}\rangle =\int^{\infty }_0{}4\pi {\cdot V_{rel}}^3\cdot {\left(\frac{\mu }{2\pi k_BT}\right)}^{\frac{3}{2}}

ParseError: invalid DekiScript (click for details)

\cdot \partial V_{rel}={\left(\frac{8\cdot k_B\cdot T}{\pi \cdot \mu }\right)}^{\frac{1}{2}} \nonumber \]

The only difference between the average velocity $\langle v\rangle = \left(\frac{8\cdot k_B\cdot T}{\pi\cdot m}\right)^{\frac{1}{2}}$ and the average relative velocity above is just an alternate definition of the mass! Notice that the relative velocity is bigger (by $\sqrt{2}$) than the vs. laboratory velocity if the masses are equal ($m_a = m_b$).

10.4.1 Collision frequency and mean free path. Here we present an interesting use of the relative velocity, which is the collision frequency and mean free path among gas particles. To calculate the collision frequency, we have to use the phenomenological model shown in Figure 10.8. The purpose is to derive an expression for what is called a “collision volume”. This is a space that, if occupied by two molecules, then they must have collided because there isn’t enough room for them not to do so. As we see in Figure 10.8, the gas molecule has a diameter d that creates a collisional cross-sectional area of $A = \pi d^2$. In Δt amount of time the gas moves over a distance $\Delta t\cdot\langle V_{rel}\rangle$, which allows us to define the collision volume:

$$\Delta t\cdot\langle V_{rel}\rangle\cdot A = \Delta t\cdot\left(\frac{8\cdot k_B\cdot T}{\pi\cdot\mu}\right)^{\frac{1}{2}}\cdot\pi d^2$$

If we simply multiply this volume by the number density $\frac{N}{V}$ then we know how many collisions occur between gas molecules over a timescale. The collision frequency, usually abbreviated Z, is thus the number of collisions per unit time: $Z = \frac{N}{V}\cdot\left(\frac{8\cdot k_B\cdot T}{\pi\cdot\mu}\right)^{\frac{1}{2}}\cdot\pi d^2$. As we showed in the calculation of flux:$fracNV = fracPk_B\cdot T$ so the above can be expressed as:

$$Z = \frac{P}{k_B\cdot T}\cdot\left(\frac{8\cdot k_B\cdot T}{\pi\cdot\mu}\right)^{\frac{1}{2}}\cdot\pi d^2$$

From this we see that larger molecules will hit each other more often, although larger molecules may weigh more which will also slow down the collision frequency. Gases under higher pressure collide more. Finally, we can also use collision frequency to determine how far a gas can travel before it hits another. This is the mean free path, called λ, which is $\lambda = \frac{\langle v\rangle}{Z} = \frac{\langle v\rangle}{\frac{P}{k_B\cdot T}\cdot\langle V_{rel}\rangle\cdot\pi d^2}$. You may recall that $\frac{\langle v\rangle}{\langle V_{rel}\rangle} = \frac{1}{\sqrt{2}}$ for a homogeneous gas, which makes:

$$\lambda = \frac{k_B\cdot T}{\sqrt{2}\cdot\pi d^2\cdot P}$$

Given the 0.346 nm diameter of oxygen, the collision frequency for O_2 at room temperature and pressure is 5.8 $\times 10^9$ s^{-1}, which makes it’s mean free path 76 nm. This is relatively far compared to the size of the molecule, which is why the “perfect” non-interacting description of gas molecules is fairly accurate.

10.5: Appendix - Jacobians

Appendix: Jacobians

A.1. 3D to 1D

A Jacobian is a mathematical entity used to switch partials inside an integral. For the case of velocity in three dimensions being converted into spherical coordinates, where v is the net velocity and akin to a sphere's radius:

\[\partial v_x\cdot \partial v_y\cdot \partial v_z=\left|\frac{\partial (v_x,v_y,v_z)}{\partial (v,\theta ,\phi)}\right|\cdot \partial v\cdot \partial \phi \cdot \partial \theta =v^2\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot \partial v\cdot \partial \phi \cdot \partial \theta \nonumber \]

To evaluate the above, we should have some idea how to convert v$_x$ v$_y$ v$_z$ into spherical coordinates to begin with. It's just a lesson in geometry:

\[v_x=v\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (theta)v_y=v\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (theta)v_z=v\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (phi) \nonumber \]

where $v=\sqrt{v_x^2+v_y^2+v_z^2}$. The Jacobian $\left|\frac{\partial(v_x,v_y,v_z)}{\partial(v,\theta,\phi)}\right|$ is the absolute values of the determinant of the following matrix:

\[\left|

UndefinedNameError: reference to undefined name 'det' (click for details)

detleft[\frac{∂v_x}{\partial v}frac{∂v_x}{\partial \theta }frac{∂v_x}{\partial \varphi }frac{∂v_y}{\partial v}frac{∂v_y}{\partial \theta }frac{∂v_y}{\partial \varphi }frac{∂v_z}{\partial v}frac{∂v_z}{\partial \theta }frac{∂v_z}{\partial \varphi }right]right| \nonumber \]

In our coordinate system the absolute value of the determinant of the matrix is:

\[\left|

UndefinedNameError: reference to undefined name 'det' (click for details)

detleft[

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (theta)\ -v

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (theta)\ v

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (phi)

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (theta)\

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (theta)\ v

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (theta)\ v

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (phi)

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (theta)\

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (phi)\ 0\ -v

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)right]right| \nonumber \]

\[=\left|-v^2(phi)(theta)-v^2

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)(phi)(theta)+0-v^2(phi)(theta)-0-v^2

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)(phi)(theta)\right|=\left|-v^2(phi)((theta)+(theta))-v^2

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)(phi)((theta)+(theta))\right|=\left|-v^2(phi)-v^2

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)(phi)\right|=\left|-v^2

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)((phi)+(phi))\right|=\left|-v^2

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\right| \nonumber \]

Since we take the absolute value of this result (the negative sign goes away), the final answer is: \(\partial v_x\cdot \partial v_y\cdot \partial v_z=v^2\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot \partial v\cdot \partial \phi \cdot \partial \theta\)

When we apply the Jacobian to the Maxwell-Boltzmann formula we see that (bold emphasis added):

\[{\left(\frac{m}{2\cdot \pi \cdot k_B\cdot T}\right)}^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot \partial v_x\cdot \partial v_y\cdot \partial v_z={\left(\frac{m}{2\cdot \pi \cdot k_B\cdot T}\right)}^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot v^2\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot \partial v\cdot \partial \phi \cdot \partial \theta \nonumber \]

Now we can integrate out the angles:

\[{\left(\frac{m}{2\cdot \pi \cdot k_B\cdot T}\right)}^{\frac{3}{2}}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot v^2\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot \partial v\cdot \int^{2\pi }_0{}

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot \partial \phi \cdot \int^{\pi }_0{}\partial \theta \nonumber \]

which leaves us with just a constant:

\[\int^{\pi }_0{}

UndefinedNameError: reference to undefined name 'sin' (click for details)

sin\ (phi)\cdot \partial \phi \cdot \int^{2\pi }_0{}\partial \theta ={-

UndefinedNameError: reference to undefined name 'cos' (click for details)

cos\ (phi)]}^{\pi }_0\cdot 2\pi =4\pi \nonumber \]

leaving us with:

$$4\pi \cdot v^2 \cdot \left(\frac{m}{2\cdot \pi \cdot k_B \cdot T}\right)^{\frac{3}{2}} \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B \cdot T}} \cdot \partial v$$

This is the velocity form of the Maxwell-Boltzmann equation.

A.2.

$\partial v_a \cdot \partial v_b \rightarrow \partial G \cdot \partial V_{rel}$ **:** The following Jacobian was used in the calculation of relative velocity:

$$\partial v_a \cdot \partial v_b = \left|\frac{\partial (v_a, v_b)}{\partial (G, V_{rel})}\right| \cdot \partial G \cdot \partial V_{rel}$$

The determinant is:

\left|\frac{\partial (v_a,v_b)}{\partial (G,V_{rel})}\right|=\left|det\left[\frac{\partial v_a}{\partial V_{rel}}frac{\partial v_a}{\partial G}frac{\partial v_b}{\partial V_{rel}}frac{\partial v_b}{\partial G}right]\right| \nonumb

Given that $v_a = G + \frac{m_b}{m_a+m_b} V_{rel}$ and $v_b = G - \frac{m_a}{m_a+m_b} V_{rel}$, we can fill out the matrix:

\left|det\left[\frac{m_b}{m_a+m_b}\ 1\ -\frac{m_a}{m_a+m_b}\ 1right]\right|=\frac{m_b}{m_a+m_b}+\frac{m_a}{m_a+m_b}=\frac{m_a+m_b}{m_a+m_b}=1 \nonumber

Done!

CHAPTER OVERVIEW

11: Boltzmann Statistics

The Boltzmann probability distribution that was introduced in Chapter 10 has many applications that describe everyday physical phenomena. These include some of the thermodynamic principles such as the Equipartition Theorem, and why vibrations don't account towards degrees of freedom in the same. Here, we will use the Boltzmann distribution to describe the lightbulb, specifically the white light spectrum and how energy efficient they are (hint: they are not energy efficient). Also we will study the heat capacity of solids, insights into which led to the development of quantum theory.

11.1: The Black body Radiator

We will begin with exploring the marvelous complexity of the wonder of nature known as the lightbulb. There are some technicalities that must be employed, which is why this derivation is generally referred to as the “black body radiator” problem. This means that we are describing an object that is hot, and self-contained like an empty box. The interior is perfectly black, causes any photons that come into existence to be re-absorbed. The fact that light photons, which have an energy $h\nu = \frac{hc}{\lambda}$ (where h is Planck’s constant 6.626×10^{-34} J·s,nu is the frequency of light, c is the speed of light and$lambda$ is the wavelength), do not escape results in the system maintaining thermal equilibrium. This is sensible because, if the photons got out, the box would cool. Nonetheless, we do have to drill a small hole into the side to see what is going on, which means that we measure the number and wavelengths of all the photons inside of it as shown in Figure 11.1A. The best way to measure emission is to record the spectrum, which would vary with the equilibrium temperature as shown in Figure 11.1.B. What is interesting is how the intensity at first rises with decreasing wavelength (increasing energy), maximizes and then rapidly falls off. Also, the spectrum of a ~5000K black body is nearly identical to the sun. This gives us a hint about the first step of our approach, which is that we must think about what kinds of wavelengths of photons fit inside the black body box to begin with.

11.1.1 Wavelength

Shown in Figure 11.2A are some representations about how light might fit inside the box of length L, which serves to dictate the wavelength of the box. These are the first four “allowed” wavelengths in the x-direction, and note how Figure 11.2.B shows that there are three directions since the Universe is three dimensional. Looking back to Figure 11.2.A we see that the first allowed photon has an infinite wavelength. While this seems odd, it is ok due to a sort of technicality because it has no energy and thus doesn’t actually exist. It “counts” because there can be non-zero wavelengths components in the y- or z- directions; this will be more clear later on. Next, we see that the next allowed wavelength has \lambdaup=2L, then L, followed by 2L/3, which clearly reveals the empirical relationship:

$$\lambda = \frac{2L}{n_x},\ n_x = 1,\ 2,\ 3\ldots$$

where n_x is called the “mode number”, which represents the #nodes-1 of the confined radiation. As you can see, increasing the mode number shortens the wavelength and raises the energy of the photon. There are mode numbers in the y- and z- directions, which can form a set $\{\mathrm{n}_x, \mathrm{n}_y, \mathrm{n}_z\}$ sort of like a vector. For example, we can describe the highest energy photon in Figure 11.2A as $\{3,0,0\}$ since there are no components of the wavelength in the y- and z- directions. There can be, as you can have mode number sets such as $\{3,1,1\}$ etc.

Now that we have a relationship that defines the wavelengths, we can determine a mathematical function to represent them, which is proposed to be:

$$E\left(x,y,z\right) = sin\left(\frac{n_x\pi}{L}\cdot x\right)\cdot sin\left(\frac{n_y\pi}{L}\cdot y\right)\cdot sin\left(\frac{n_z\pi}{L}\cdot z\right)$$

where E is the electric field of the photons. You can verify that these are the proper representation for the waves that have corresponding mode numbers such as those shown in Figure 112.

At this point in your academic career you should be aware that a photon is an oscillating electric and magnetic fields. The ability of light’s electric component to perturb objects and impart force is significantly greater than the magnetic field, so we usually don’t need to describe the magnetic properties of light. Regardless, the fact that electromagnetism has entered the discussion means that we now need to examine whether our relationship conforms to Maxwell’s Equations, which are laws that govern all electromagnetism phenomena including light itself. As it applies here, what happens is that when we apply Gauss’s Law to the equation, we can derive , which is known as the wave equation.

$$\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z}\right\} E\left(x,y,z,t\right) = \frac{-1}{c^2}\frac{\partial^2}{\partial t^2}E\left(x,y,z,t\right)$$

When we insert our relationship we find:

$$E\left(y,z,t\right)\frac{\partial^2}{\partial x^2}sin\left(\frac{n_x\pi}{L}\cdot x\right)+E\left(x,z,t\right)\frac{\partial^2}{\partial y^2}sin\left(\frac{n_y\pi}{L}\cdot y\right)+E\left(x,y,t\right)\frac{\partial^2}{\partial z}sin\left(\frac{n_z\pi}{L}\cdot z\right)$$
$$=E\left(x,y,z\right)\frac{1}{c^2}\frac{\partial^2}{\partial t^2}sin\left(\frac{2\pi c}{\lambda}\cdot t\right)$$

We can evaluate terms such as:

$$E\left(y,z,t\right)\frac{\partial^2}{\partial x^2}sin\left(\frac{n_x\pi}{L}\cdot x\right)=-\frac{n_x^2\pi^2}{L^2}E\left(x,y,z,t\right)$$

Which makes:

$$E\left(x,y,z,t\right)\left\{\frac{n_x^2\pi^2}{L^2}+\frac{n_y^2\pi^2}{L^2}+\frac{n_z^2\pi^2}{L^2}\right\}=E\left(x,y,z,t\right)\frac{4\pi^2}{\lambda^2}$$

The equation for the electric field can be divided out on the left and right sides leaving:

$$\frac{\pi^2}{L^2}\left(n_x^2+n_y^2+n_z^2\right)=\frac{4\pi^2}{\lambda^2}$$

If we simply treat the mode set like a vector, which has a net value:

$$n^2=n_x^2+n_y^2+n_z^2$$

then the above simplifies to:

$$\lambda^2=\frac{4L^2}{n^2}orlambda=\frac{2L}{n}$$

One important aspect of this result is that it demonstrates that mathematical models can tell us more than what the model is.

11.1.2 Mode Degeneracy

We now can relate the wavelengths that fit inside the box to the net mode number n. These values are discrete, since n is composed of a combination of whole numbers as shown in Table 11.1. To visualize, we can think of the spectrum of emission as being composed of posts that can accommodate a stack disks; each post is positioned to represent an allowed wavelength, and the disks are photons that reside at those wavelengths. Technically, each post can hold one disk, and each disk represents two photons since light comes right and left circularly polarized form. This idea is illustrated in Figure 11.3. However, there is a slight complication. Take for example that for the net mode number of $n=1$ corresponding to a wavelength of $\lambda=2L$. There are actually three sets of $\{$n$_x$, n$_y$, n$_z\}$ that given$n=1$; they are \left\{1,0,0\right\},left\{0,1,0\right\} and $\{0,1,0\}$. Likewise a mode number of $n=\sqrt{2}$ can also come about from three sets, \left\{1,0,1\right\},left\{1,1,0\right\} and $\{0,1,1\}$. However, $n=\sqrt{3}$ can only come about from $\{1,1,1\}$, and there is no combination of whole mode numbers that provide $n=\sqrt{7}$.

$n^2 = n_x{}^2 + n_y{}^2 + n_z{}^2$	$\{n_x, n_y, n_z\}$	Number of sets (degeneracy)
1	{1,0,0},{0,1,0},{0,0,1}	3
2	{1,1,0},{0,1,1},{1,0,1}	3
3	{1,1,1}	1
4	{2,0,0},{0,2,0},{0,0,2}	3
5	{0,1,2},{0,2,1},{1,0,2},{2,0,1},{1,2,0},{2,1,0}	6
6	{1,1,2},{1,2,1},{2,1,1}	3
7	**No examples**	-
8	{2,2,0},{0,2,2},{2,0,2}	3

$n^2 = n_x{}^2 + n_y{}^2 + n_z{}^2$	$\{n_x, n_y, n_z\}$	Number of sets (degeneracy)
9	{1,2,2},{2,1,2},{2,2,1},{0,0,3},{0,3,0},{3,0,0}	6
10	{0,1,3},{0,3,1},{1,0,3},{3,0,1},{1,3,0},{3,1,0}	6
⋮	⋮	⋮
10,800	{60,60,60},{20,76,68},…	28
⋮	⋮	⋮
24,300	{90,90,90},...	91

Table 11.1. How net mode numbers n^2 can be composed of multiple whole number $\{n_x, n_y, n_z\}$ sets.

The reason that the emission spectrum initially rises with decreasing wavelength as seen in Figure 11.1B is because of how the number of sets that yield the same net mode number is generally increasing as seen in Table 11.1 and Figure 11.3. Since the net mode number corresponds to a specific wavelength and thus energy of light, the number of sets is the degeneracy of the energy state. Now our purpose here is to generate a relationship between the net mode number and the degeneracy.

Unfortunately, as can be seen in Table 11.1 there isn't a simple formula that can take n or n^2 as an input and generate the degeneracy as the output. This can be visualized in 2D as shown in Figure 11.4, where we represent n as the radius of a circle on a graph of n_y vs. n_x. Each red cross represents distinct mode set, but we can see that a semi-circle of radius n doesn't cross many of them. In fact, it doesn't seem clear that there is a simple formula that relates the net mode number n to the number of nearby modes. However, as shown in Figure 11.4B, any particular point $\{n_x, n_y\}$ is offset from every other point by $\Delta n_x = \pm 1$ and/or $\Delta n_y = \pm 1$. As a result, we can say that each mode number occupies an area on the graph of $1^2 = 1$. Since one point occupies an area of 1, we now have a way to count up mode sets as a function of the net mode number n. This is easy because n looks just like a radius when plotted against n_x and n_y as in Figure 11.4C, and we can define an area associated with n using a quarter disk with a thickness of ∂n. Hence the degeneracy for the 2D system can be calculated via the area of a quarter disk, which is the circumference times the thickness:

$$2D\ degeneracy(n) = \left(\frac{1}{4}\right) 2\pi n \cdot \partial n$$

Of course, we live in three dimensions. Since $1^3 = 1$, we can imagine that the 3D degeneracy can be calculated by volume. In fact, if the number of degeneracies in 2D is 1/4th the area of a disk, then for 3D the degeneracy is 1/8th the volume of a shell:

$$3D\ degeneracy(n) = \left(\frac{1}{8}\right) 4\pi n^2 \cdot \partial n$$

where the shell volume is the surface area of a sphere ($4\pi n^2$) times the shell's thickness ∂n. To make further progress we have to remove the mode number n and insert \lambdaup, since spectrometers report on wavelength. Earlier, when we applied Maxwell's equations to the equation for the electric field of light we found that: $\lambda^2 = \frac{4L^2}{n^2}$ and therefore $n^2 = \frac{4L^2}{\lambda^2}$. Making this substitution into the above reveals:

$$3D\ degeneracy(n) = \left(\frac{1}{8}\right) 4\pi \frac{4L^2}{\lambda^2} cdot\partial n = \frac{2\pi L^2}{\lambda^2} cdot\partial n$$

Two more problems; we have to multiply the above by 2 to represent the fact that light has both left and right circularly polarized forms. Also, we have to convert ∂n to $\partial \lambda$ using a Jacobian: $\partial n \rightarrow \left|\frac{\partial n}{\partial \lambda}\right| \partial \lambda$:

\[3D\ degeneracy(\lambda)=2\times \frac{2\pi L^2}

ParseError: invalid DekiScript (click for details)

{\partial \lambda }\right|\partial \lambda =\frac{8\pi L^3}{{\lambda }^4}partial \lambda \nonumber \]

This is the analytical result plotted in Figure 11.3. Ultimately, we see that shorter wavelength photons "fit" into the black box better and thus have more degeneracies, which increases the light output from a bulb as seen in Figure 11.1.B. However, if the wavelength becomes too short then the intensity of light drops off, which is to say that there appears to be some sort of high energy cutoff. This suggests that the Boltzmann equation plays a role, since nature doesn't partition out energy into things if that energy is greater than k_BT.

11.1.3 Total Energy

Now that we have an expression for the degeneracy of light modes in the black body radiator, we can now calculate the total energy from a lightbulb using:

$$Total\ Energy = \sum_{\lambda} degeneracy(\lambda) \cdot \langle energy\,(\lambda)\rangle$$

Here we see that we need to calculate the average energy of the lightbulb's mode as a function of the mode's wavelength, $\langle energy\,(\lambda)\rangle$. We are already well aware that the energy of a photon is $\frac{h\cdot c}{\lambda}$, and with this we can apply the Boltzmann equation to calculate the average. A subtlety is revealed at this point- how is the energy of the photon dialed up or down to conform to the Boltzmann equation? Afterall, to calculate the energy at a defined wavelength using $\frac{h\cdot c}{\lambda}$, everything is a constant (h is the Plank constant, 6.626×10^{-34} J•s, and c is the speed of light)! It turns out that the Boltzmann formula is satisfied by varying the *number* of photons, to which we now use in the equation:

$$P\left(\frac{j\cdot h\cdot c}{\lambda}\right) = \frac{e^{\frac{-Energy}{k\cdot T}}}{\sum e^{\frac{-Energy}{k\cdot T}}} = \frac{e^{\frac{-j\cdot h\cdot c}{\lambda\cdot k_BT}}}{\sum_{i=0}^{\infty} e^{\frac{-i\cdot h\cdot c}{\lambda\cdot k_BT}}}$$

where $P\left(\frac{j\cdot h\cdot c}{\lambda}\right)$ is the probability density for having j photons of wavelength λ given temperature T. First thing we do is to solve the normalizer (i.e. the denominator), $\sum_{i=0}^{\infty} e^{\frac{-i\cdot h\cdot c}{\lambda\cdot k_BT}}$. The summation reflects the fact that Nature can dictate that there are as little as 0 photons and as many as ∞. To solve this part, we can use the following identity:

$$\sum_{i=0}^{\infty} a^i = \frac{1}{(1-a)}; i = 0, 1, 2, 3\ldots$$

This works because the number of photons is discrete, i.e. there can only be whole numbers (0, 1, 2, 3, ...) of them. Applying the identity means: $a = e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}$, which makes:

$$\sum_{i=0}^{\infty} e^{\frac{-i\cdot h\cdot c}{\lambda\cdot k_BT}} = \frac{1}{\left(1 - e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)}$$

Now we can try to deal with the average energy via:

$$\langle energy\rangle = \sum energy \cdot Boltzmann\ distribution = \sum_{j=0}^{\infty}\left(\frac{j\cdot h\cdot c}{\lambda}\right)\cdot\left(1 - e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right) e^{\frac{-j\cdot h\cdot c}{\lambda\cdot k_BT}}$$

where: $\left(\frac{j\cdot h\cdot c}{\lambda}\right)$ is the energy of a j number of \lambdaup—wavelength photons and: $\left(1 - e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right) e^{\frac{-j\cdot h\cdot c}{\lambda\cdot k_BT}}$ is the normalized Boltzmann distribution. To solve the expression above we use the following identity:

$$\sum_{i=0}^{\infty} i\cdot a^i = \frac{a}{(1-a)^2};\ i = 0, 1, 2, 3\ldots$$

Applying the identity above to $\sum_{j=0}^{\infty}\left(\frac{j\cdot h\cdot c}{\lambda}\right)\cdot e^{\frac{-j\cdot h\cdot c}{\lambda\cdot k_BT}}\cdot\left(1 - e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)$, we need to identify the constants: $\frac{h\cdot c}{\lambda}\cdot\left(1 - e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)$ and: $a = e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}$. Thus, the average energy is:

$$\sum_{j=0}^{\infty}\left(\frac{j\cdot h\cdot c}{\lambda}\right)\cdot e^{\frac{-j\cdot h\cdot c}{\lambda\cdot k_BT}}\cdot\left(1-e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)=\left(\frac{h\cdot c}{\lambda}\right)\cdot e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\cdot\frac{\left(1-e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)}{\left(1-e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)^2}$$

This is:

$$\langle energy\rangle=\left(\frac{h\cdot c}{\lambda}\right)\cdot\frac{e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}}{\left(1-e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)}$$

Now we can simplify further by this neat trick of multiplying the top and bottom by $e^{\frac{h\cdot c}{\lambda\cdot k_BT}}$:

$$\left(\frac{h\cdot c}{\lambda}\right)\cdot\frac{e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}}{\left(1-e^{\frac{-h\cdot c}{\lambda\cdot k_BT}}\right)}\cdot\frac{e^{\frac{h\cdot c}{\lambda\cdot k_BT}}}{e^{\frac{h\cdot c}{\lambda\cdot k_BT}}}=\left(\frac{h\cdot c}{\lambda}\right)\cdot\frac{e^{0}}{\left(e^{\frac{h\cdot c}{\lambda\cdot k_BT}}-e^{0}\right)}=\frac{h\cdot c}{\lambda\cdot\left(e^{\frac{h\cdot c}{\lambda\cdot k_BT}}-1\right)}$$

Done! The average energy of a \lambdaup-wavelength photon is:

$$\langle energy\,(\lambda)\rangle=\frac{h\cdot c}{\lambda\cdot\left(e^{\frac{h\cdot c}{\lambda\cdot k_BT}}-1\right)}$$

This result is plotted in Figure 11.5, where we can see that the average energy rises with increasing wavelength. This is sensible, because if the energy of a photon is on the order of k_BT (or less), Nature allows you to have more of those photons.

We can now finally solve for the total energy output of a lightbulb and calculate the spectrum at the same time. Shown in Figure 11.5 is a representation of the average energy as a stack of discs that correlates to the number of photons. The modes and degeneracies of the blackbody were previously presented as a series of posts to stack the photon discs on. Now we see the reason that a lightbulb's spectrum rises and falls with increasing wavelength- Nature provides the energy to create more photons as the energy per photon drops with increasing wavelength. However, the photons must also reside in blackbody radiator modes, which decrease with increasing wavelength. The result is a rise and fall of intensity, which mimics the spectra shown in Figure 11.1.

Now to create a mathematical representation of the same. First, we return to our original expression for the total energy:

$$Total\ Energy=\sum_{\lambda}degeneracy(\lambda)\cdot\langle energy\,(\lambda)\rangle$$

Technically, the above result is dependent on the volume of the lightbulb, as a bigger bulb produces more energy. We should instead present the result as the energy density, the total energy divided by the volume, which can be applied to any sized black box radiator:

$$Energy\ Density=\frac{Total\ Energy}{Volume}=\frac{1}{L^3}\sum_{\lambda}degeneracy(\lambda)\cdot\langle energy(\lambda)\rangle$$

We insert the relationships derived above, and then we can approximate the wavelengths as varying continuously. This allows us to change the sum to an integral; we also do some algebraic cleaning:

$$Energy\ Density=\left(\frac{1}{L^3}\right)\int_0^{\infty}\left(\frac{8\pi L^3}{\lambda^4}\right)\cdot\frac{h\cdot c}{\lambda\cdot\left(e^{\frac{h\cdot c}{\lambda\cdot k_BT}}-1\right)}\cdot\partial\lambda=\int_0^{\infty}\frac{8\pi\cdot h\cdot c}{\lambda^5\cdot\left(e^{\frac{h\cdot c}{\lambda\cdot k_BT}}-1\right)}\cdot\partial\lambda$$

where the expression:

$$\frac{8\pi\cdot h\cdot c}{\lambda^5\cdot\left(e^{\frac{h\cdot c}{\lambda\cdot k_BT}}-1\right)}$$

is known as the Planck distribution and is exactly what is plotted in Figure 11.1B. Last, we evaluate the integral above, which unfortunately is rather difficult and requires a bit of sophistication to derive. Regardless, the result is:

$$\frac{8\pi^5 (k_B T)^4}{15 (h \cdot c)^4}$$

and is known as the **Stefan–Boltzmann law**.

11.2: Heat Capacity of Solids

In the early 1800's French scientists Pierre Dulong and Alexis Petit noticed that many solid elements had near-identical per molar heat capacities as shown in Figure 11.6. This led to the Dulong–Petit law: $C_m = 3R$. Previously in Ch. 2 we encountered gases with such high heat capacities due to their three translational and three rotational motions, which imparts six degrees of freedom that rendered $C_m = 3R$ due to the equipartition theorem (Table 2.1). While this is perfectly understandable for a gas, it's hard to reconcile why heavy metallic elements such as lead and a gas such as methane have the same heat capacities. The answer is simple-solids have three (vibrational) potential energy and three kinetic energy degrees of freedom due to their bonding. Thus, the equipartition theorem still appears valid for solids, unless, those solids are cold, in which case something goes terribly wrong as shown in Figure 11.7.

From the data in Figure 11.7 we can see that, at low temperatures, solids of copper and tungsten have almost no heat capacity! And while it rises with temperature to the Dulong-Petit limit, it was quite the curiosity for many years why this behavior was observed in many materials. In fact, it was one of Albert Einstein's early contributions in 1907 to approximately describe the increase in heat capacity as vibrations in the solid state, called phonons, that behave just like Planck's photons. In this regard, instead of energy being related to the wavelength of light it was due to the frequency of an atomic vibration in the solid state. All one has to do is simply change the definition of average internal energy (U), as derived from the Boltzmann formula, from the Planck to the Einstein form: \(\frac{h\cdot \frac{c}{\lambda }}{e^{\frac{\hslash \cdot c}

ParseError: invalid DekiScript (click for details)

-1}\to 3N_A\cdot \frac{\hslash \omega }{e^{\frac{\hslash \omega }{k_BT}}-1}\). The prefactor is due to solids existing in 3 dimensions and that a mole has N_A number of atoms, and note that Einstein assumed that all the vibrations inside the solid had the same frequency ω. Since heat capacity is just the derivative of the internal energy with temperature, the result is:

\[C=3N_A\cdot \frac{\partial }{\partial T}\left(\frac{\hslash \omega }{e^{\frac{\hslash \omega }{k_BT}}-1}\right)=3N_A\cdot \frac{-\hslash \omega }

ParseError: invalid DekiScript (click for details)

{\partial T}=3N_A\cdot \frac{-\hslash \omega }

ParseError: invalid DekiScript (click for details)

=3N_Ak_B{\left(\frac{\hslash \omega }{k_BT}\right)}^2\frac{e^{\frac{\hslash \omega }{k_BT}}}{{\left(e^{\frac{\hslash \omega }{k_BT}}-1\right)}^2} \nonumber \]

This result correctly predicts that, as T→0 K, the heat capacity also →0 J/K/mol. At higher temperatures where: $e^{\frac{\hbar\omega}{k_BT}} \sim 1+\frac{\hbar\omega}{k_BT}$ we find that:

$$C \sim 3N_A k_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{1+\frac{\hbar\omega}{k_BT}}{\left(\frac{\hbar\omega}{k_BT}\right)^2} \sim 3N_A k_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \left(\frac{k_BT}{\hbar\omega}\right)^2 = 3N_A k_B = 3R$$

All of these results make us believe that Einstein has the correct approach; however, this turns out not to be the case! The problem is that the heat capacity rises exponentially in the Einstein model whereas in reality most materials have a $C_{p,m}$~T^3 behavior. And as shown by Peter Debye in 1912 this was due to Einstein's use of a single frequency for the solid-state vibrations, whereas there are a range of frequencies as shown in the inset of Figure 11.7.

The solution to address concerning the shortcoming of the Einstein model is to use a range of phonon frequencies to define the internal energy as so:

$$U = \int degeneracy\left(\omega\right) \cdot \left\langle energy\left(\omega\right)\right\rangle = \int degeneracy\left(\omega\right) \cdot \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}}-1}\partial\omega$$

So as not to labor the point one can show that the degeneracy of phonons as a function of frequency is $\frac{V\omega^2}{2\pi^2 v_s^3}$, where v_s is the speed of sound in the solid. As a result the Debye equation for the heat capacity of a solid is: $C = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\frac{V\omega^2}{2\pi^2 v_s^3}\int_0^{\omega_D}\frac{V\omega^2}{2\pi^2 v_s^3}\frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_BT}}-1}\partial\omega \propto T^3$

While we don't need to worry further about the mathematics of the result, suffice to say the result is proportional to T^3 as experimentally observed. It is also interesting to note that the upper limit of the Debye equation isn't infinity as one might expect. This is because Debye realized that there was an upper limit to the range of phonon frequencies as shown in Figure 11.8, which we will call the Debye frequency ω_D. Clearly, there cannot be a frequency higher than allowed by the atomic spacing. In practice, this upper limit is an empirical parameter that can be used to create a fit to experimental data.

Conclusion. The purpose of this chapter was to demonstrate that the Boltzmann formula has uses far beyond that encountered with the Maxwell-Boltzmann description of the velocities of gases. In terms of the development of physical chemistry as a science, it wasn't long after the phenomena of Blackbody radiation and the Debye theory of heat capacity were described that scientists started to make the connection between matter and waves. This ultimately resulted in quantum theory, which is the subject of the next chapter.

CHAPTER OVERVIEW

12: Introduction to the Schrödinger Equation

12.1: Einstein’s Theory of Relativity

Occasionally mainstream news, whether TV or internet, like to report on scientific phenomena and recent findings. However, they invariably simplify things to the point that the information is wrong. The two greatest victims of these unfortunate oversimplifications are the theories of relativity and quantum mechanics. For example, $E = mc^2$ anyone? Not hardly, Einstein derived the following:

$$E^2 = c^2p^2 + m^2c^4$$

where E is energy, m is mass, c is the speed of light, and p is momentum. The above is clearly a mouthful; however, if the particle isn’t moving (p=0), then $E^2 = m^2c^4$ which simplifies to:

$$E = mc^2$$

Thus, this ultra-famous equation is only correct for a particle at rest. And as you will see shortly, quantum mechanics stipulates that everything is always moving.

Einstein’s equation provides a launching point for the development of quantum mechanics. In this regard, let’s say that we are studying a particle with no mass such as a photon ($m = 0$ kg). In that case:

$$E^2 = c^2p^2 \rightarrow E = cp$$

The energy of a photon is known to be $h\upsilon$, where h is Planck’s constant and υ is frequency which is: $\upsilon = \frac{c}{\lambda}$ and λ is the wavelength. We can thus show that $E = h\frac{c}{\lambda} = \ cp$, which means that a massless particle such as a photon has a momentum: $p = \frac{h}{\lambda}$. Even though momentum is mass times velocity, and a photon has no mass, it still has a momentum. And now you should also know that many of the things you were told were absolutely true are, in fact, not true at all. Also, this is just our beginning of the discussion of Stranger Things.

12.1.1 Why waves?

The theory of small things introduces concepts that seem preposterous to those indoctrinated into classical mechanics, defined as Isaac Newton’s equation:

force = mass × acceleration.

It should be made clear on the outset that the theory of quantum mechanics as formulated by the Schrödinger equation is known to be incorrect. However, for chemistry the form of quantum mechanics introduced here is as accurate as can be measured, so its “good enough” for developing a thorough understanding of chemical phenomena.

The most important concept is that small things (mostly electrons) often act more like waves than particles. For example, if a truck hits a wall, it will break through it if it is travelling fast enough (or faster than that!). However, if the truck is actually an electron, it may break through the wall even if it is going very slowly. Alternatively, if it has the right speed to break through the wall, it might instead just bounce off it. Confused yet? Here is a better analogy- an electron trying to get through a barrier is like light skimming off the surface of water. And that is because of the wave equation.

12.2: The Schrödinger Equation

We started to understand waves once Maxwell's equations for electromagnetism were developed. They are:

$$\nabla \times \mathcal{E} = -\frac{\partial B}{\partial t}$$

$$\nabla \times B = \frac{1}{c^2}\frac{\partial \mathcal{E}}{\partial t}$$

$$\nabla \mathcal{E} = 0$$

$$\nabla B = 0$$

where $\mathcal{E}$ and B are electric and magnetic fields and t is time. You worked with these equations when you took Physics II to understand how an oscillating magnetic field creates electricity (alternatively, how an electric motor spins). You probably had to calculate the electric field from a dipole as well. The wave equation comes about when you combine these equations to show that:

$$\frac{\partial^2}{\partial x^2}\mathcal{E} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$$

A function for the electric field $\mathcal{E}$ that can solve the above is: $\mathcal{E}(x,t) = \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$, where ω is the angular frequency ($\omega = 2\pi\nu$). This describes a wave travelling to the right. If we input this function into: $\frac{\partial^2}{\partial x^2}\mathcal{E} = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}$, and by calculating the double derivatives we can show that:

$$\frac{\partial^2}{\partial x^2}\cos\left(\frac{2\pi}{\lambda}x - \omega t\right) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$$

And therefore:

$$\left(\frac{2\pi}{\lambda}\right)^2 \cos\left(\frac{2\pi}{\lambda}x - \omega t\right) = \frac{\omega^2}{c^2}\cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$$

Since you can eliminate the function $\cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$ from both sides the remainder is: $\left(\frac{2\pi}{\lambda}\right)^2 = \frac{\omega^2}{c^2}$, and thus $\lambda\omega = 2\pi c$. This is a well-known description of how wavelength and frequency of light are related.

Here we will examine how to adjust the parameters of the wave equation to include mass, which will lead us to quantum mechanics for particles. If we look back at: $\mathcal{E}(x,t) = \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$, we can multiply and divide the argument of cosine by the Plank constant h:

$$\mathcal{E} = \cos\left[\frac{1}{h}\left(\frac{2\pi h}{\lambda}x - h2\pi\nu t\right)\right]$$

If we introduce a new constant $\hbar = \frac{h}{2\pi}$, we have:

$$\cos\left[\frac{1}{\hbar}\left(\frac{h}{\lambda}\cdot x - h\nu\cdot t\right)\right]$$

where we see the formula for momentum $p = \frac{h}{\lambda}$ from the discussion on relativity in the previous section and we of course know that $h\nu$ is the energy (E) of a photon (or any wave). Thus:$\psi(x,t) = \cos\left[\frac{1}{\hbar}(p\cdot x - E\cdot t)\right]$

where we have used a new symbol (ψ) to replace $\mathcal{E}(x,t)$ as we are moving further away from describing the electric field of photons. If we plug this \(\psi \left(x,t\right))wavefunction back into our starting point:

$$\frac{\partial^2}{\partial x^2}\psi = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi$$

Since $\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\psi = \frac{E^2}{\hbar^2 c^2}\psi$:

$$c^2\hbar^2\frac{\partial^2}{\partial x^2}\psi = E^2\psi$$

and as $\frac{\partial^2}{\partial x^2}\psi = \frac{p^2}{\hbar^2}\psi$ we can see that the above translates into: $c^2p^2 = E^2$. This is just Einstein's equation for energy of a massless particle! However, the point of this derivation is to introduce mass into the wave equation. To do so we look back at the real equation for relativistic energy: $c^2p^2 + m^2c^4 = E^2$ and take the square root to approximate: $\frac{p^2}{2m} + mc^2 \approx E$. The next few steps are a bit too onerous to review here; regardless, the end result is the 1-dimensional non-relativistic Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = E\psi$$

where the approximations made remove the effects of relativity; this is why the speed of light no longer appears in the equation. Since this equation is for a moving particle with no potential energy, the total energy is just kinetic, i.e. $E = \frac{p^2}{2m}$. The last thing to note is that, to extend the above to three dimensions you simply add in the double derivatives in y and z:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi = \frac{-\hbar^2}{2m}\nabla^2\psi = \frac{p^2}{2m}\psi = E\psi$$

12.2.1 Where's the potential?

In the previous derivation we never considered potential energy. Where does it go into the equation? We showed above that: $\frac{-\hbar^2}{2m}\nabla^2$ is related to: $\frac{p^2}{2m}$, which is the kinetic energy because: $\frac{p^2}{2m}$ and: $\frac{1}{2}mv^2$ are the same thing! With this knowledge it becomes more apparent that the Schrödinger equation resembles a well-known formula from freshman physics:

$$Kinetic\ Energy + Potential\ Energy = Total\ Energy$$

As a result, if we simply state that the potential energy is just a function: V(x,y,z), then the full Schrödinger equation is:

$$\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

12.1.2 Consistency with the de Broglie relation

In 1923 Louis de Broglie proposed that, if wavy light can have particle-like properties (i.e. momentum), then perhaps particles can be wavy. To this end he derived the following, starting with Einstein's equation of energy for a particle at rest: mc^2 and equating that to the energy hv of a wave:

$$mc^2 = hv$$

As the frequency of light v is related to the wavelength by: $\lambda v = c$, the energy of the wave can be converted into: $hv = h\frac{c}{\lambda}$. This means we can solve the wavelength from: $mc^2 = h\frac{c}{\lambda}$:

$$\lambda = \frac{h}{mc}$$

Since a particle with mass can't travel the speed of light, de Broglie substituted in the velocity v for the speed of light: $\lambda = \frac{h}{mv}$. Since momentum is: $p = mv$, we are left with a relationship for the wavelength of a particle as determined by its momentum:

$$\lambda = \frac{h}{p}$$

When de Broglie determined that matter has an associated wavelength in 1924 at first no one paid much attention (and likely didn't understand the implications). However, Albert Einstein noted de Broglie's work, which generated interest and as such three years later Clinton Davisson and Lester Germer were able to prove the de Broglie hypothesis by diffracting electrons off a piece of metal. Shown in Figure 12.1 is an example of electron diffraction. Normally, one would expect electrons pointing at two slits in a material to go through like bullets; they ought to simply create a shadow of the two slits on the screen behind. However, since electrons have wavelength the two slits form an interference pattern just like light through a diffraction grating. Also shown in Figure 12.1 are Davisson and Germer's original data. Vindicated, de Broglie won the Nobel Prize in 1929.

What is most interesting about the Schrödinger equation is that it can return the de Broglie hypothesis if you "ask" it properly. Hopefully, you are wondering what does it mean for an equation to "ask"? In other words, how do you tease out: $\lambda = \frac{h}{p}$ (de Broglie) from: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{p^2}{2m}\psi$ (Schrödinger)? Starting with the latter, we must insert something for ψ, which is our model for a particle. To this end we use the most simple wave equation possible, which is: $\psi = \cos\left(2\pi\frac{x}{\lambda}\right)$. This wave equation is subject to the Schrödinger equation's double derivative $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ as follows: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\cos\left(2\pi\frac{x}{\lambda}\right) = \frac{4\pi^2\hbar^2}{2m\cdot\lambda^2}\cos\left(2\pi\frac{x}{\lambda}\right)$

Since $\hbar = \frac{h}{2\pi}$:

$$\frac{4\pi^2\hbar^2}{2m\cdot\lambda^2}\cos\left(2\pi\frac{x}{\lambda}\right) = \frac{h^2}{2m\lambda^2}\psi$$

Based on the Schrödinger equation: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{p^2}{2m}\psi$, it must be true that: $\frac{h^2}{2m\lambda^2} = \frac{p^2}{2m}$. Simplifying further shows: $\lambda^2 = \frac{2m\cdot h^2}{2m\cdot p^2}$, which reveals de Broglie's wavelength $\lambda = \frac{h}{p}$.

The demonstration above reveals that the Schrödinger equation is consistent with the de Broglie relationship. It also shows that: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, which we will call an "operator" for now on, provides the kinetic energy as we presumed already. To make these types of derivations easier in the future we will simplify the wave equation as:

$$\psi = \cos\left(2\pi\frac{x}{\lambda}\right) \rightarrow \cos(kx)$$

where $k = \frac{2\pi}{\lambda}$, and is called the "wavevector". In three dimensions k is truly a vector and points in the direction that the wave is travelling in. We can determine some relationships between the wavevector k, momentum, and energy via application of the Schrödinger equation:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\cos(kx) = \frac{\hbar^2 k^2}{2m}\cos(kx) = E\cdot\cos(kx)$$

From the above it must be true that: $\frac{\hbar^2 k^2}{2m} = E$, and as a result: $k = \frac{\sqrt{2mE}}{\hbar}$ and $\psi = \cos\left(\frac{\sqrt{2mE}}{\text{\textbackslash hslashx}}\right)$. You may also notice from the above that: $p^2 = \hbar^2 k^2$, and since $k = \frac{2\pi}{\lambda}$ and $\hbar = \frac{h}{2\pi}$ we have: $p^2 = \left(\frac{h}{2\pi}\right)^2\left(\frac{2\pi}{\lambda}\right)^2$ which simplifies to the de Broglie relationship: $\lambda = \frac{h}{p}$. Everything is self-consistent!

12.3: Born interpretation

Back in the mid 1920's there was some confusion as to the purpose of the wave equation ψ. While it can deliver a numerical value for energy (quite useful), some questioned if they have any intrinsic meaning. For example, my Aunt Mary's dog only turns right when walking, hence an equation for the angle of his turns is $-|\theta|$. This implies that he tries to turn left (positive θ) an unseen force causes him to reverse (the negative of the absolute value). What do we call this doggie force? Is it fundamental, like gravity or electromagnetism, and can we measure this force acting on other dogs? *What about cats?*

In reality, the dog had surgery on his left paw and that is why he only turns right, a fact that isn't captured by $-|\theta|$. Hence, we shouldn't over interpret an equation that describes him. Are we doing the same thing with wave equations?

Max Born was the first to state that wave equations have substantial meaning, which is to say that they represent probability distributions. Specifically, if you square the wavefunction to make sure it is always positive as shown in Figure 12.2, it represents the probability that you can find the particle at some point in space (probability distributions were discussed at length in Chapter 10). The fact that the wavefunction squared is a probability distribution requires that it be "normalized", which means:

$$\int_{lower\ limit}^{upper\ limit}|\psi|^2\partial\tau=\int_{lower\ limit}^{upper\ limit}\psi^*\psi\partial\tau=1.0$$

where ψ^* is the complex conjugate of the wavefunction, which needs to be used because most wavefunctions are complex (i.e. they have $i=\sqrt{-1}$ in them). There is a substantial amount to unpack from this normalization equation. First, we didn't specify the limits because they depend on what is being represented and how "big" the wave equation is allowed to be. For example, if we are using quantum mechanics to describe a particle trapped in a box of length L, then the lower limit would likely be x=0 and the upper x=L. Also note the partial $\partial\tau$ in the integral. This is a symbol that is generic for the dimensionality of the wave equation. Thus far, we have been dealing with a wave in the x direction, so $\partial\tau=\partial x$. If we were trying to solve a quantum mechanical problem for a particle in three dimensions, then $\partial\tau=\partial x\partial y\partial z$, and of course that means that normalization integral is actually a triple integral. If we were working in radial coordinates then $\partial\tau=r^2 sin(\theta)\partial r\partial\phi\partial\theta$, where $r^2 sin(\theta)$ is the Jacobian that property accounts for the volume. If there is no angular dependence to a problem that involves radius, then $\partial\tau=4\pi r^2\partial r$. Last, you should know that we are going to have to use complex mathematics to work quantum mechanical problems. If you are not familiar, there is a short description of most of what you need to know on the next page; more can be found on the "internet". While this may seem like more to learn (and it is), the value is that complex mathematics makes solving quantum mechanical problems much easier.

12.3.1 Normalization. Let's take a look back at what it means for a wave equation to be normalized. Generally, when we determine that a wavefunction is something like: $\psi=cos(kx)$, for example, it is unlikely to be normalized. As a result, we have to make it normalized. To do so you multiply ψ by a normalization constant (N) as:

$$\psi_{norm}=N\psi=\frac{1}{\sqrt{\int|\psi|^2\partial\tau}}\psi$$

As a result:

$$\int\psi_{norm}^2\partial\tau=\frac{\int\psi^*\psi\partial\tau}{\sqrt{\int|\psi|^2\partial\tau}\sqrt{\int|\psi|^2\partial\tau}}=\frac{\int\psi^*\psi\partial\tau}{\int\psi^*\psi\partial\tau}=1$$

and clearly $N=\frac{1}{\sqrt{\int\psi^2\partial\tau}}$. It is often the case that we first figure out what kind of function (sine, cosine etc.) is the solution to the wave equation, and then normalize it after the fact. Sometimes we don't need to normalize the wave equation to answer problems, but it is a good practice. In fact, we will generally assume that wave equations have been properly normalized in our further discussions. It is interesting to note that the requirement for normalization means that not any function can be a wavefunction; in fact there are a few restrictions on solutions as discussed below.

12.3.2 Wave equation restrictions. Since the absolute value, i.e. the square of the wave equation, must be related to probability there are some restrictions on what wave equations can and cannot do as shown in Figure 12.3. First, they cannot be 0 everywhere. This is sort of silly, since $\psi=0$ doesn't leave much room for solving any problems. Second, they must be continuous. Otherwise, there are basically two probabilities for a particle to be found at a certain point in space- what kind of nonsense is that? Third, the wavefunctions must be smooth, which means that the derivative cannot approach ∞ at any point. As you will see later, if the derivative did so then the particle would have more kinetic energy that the Universe holds. Last, wavefunctions cannot be divergent, which means that they can be integrated to a finite value. If not, then the wavefunction could not be normalized, which would not be consistent with the rules of probability distributions.

One of the tricks of quantum mechanics is to use these restrictions to solve problems. Generally, the most relevant are the smooth and continuous stipulation at some sort of boundary. Often that boundary takes the form of a sudden change in the potential energy at a point in space. Another observation is that these boundary conditions mean that a solution for the wave equation can't be found for any energy, rather, often discrete energy values. This is the source of the "quantum" in quantum mechanics, and the solutions are likely to look like standing waves discussed earlier.

12.4: The Eigenvalue Equation and operators

Previously we referred to the kinetic energy part: $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ of the Schrödinger equation as an “operator”. This is a good name because the double derivative causes you to “do” something to the wave equation, i.e. you operate on it. There are many different types of operators because there has to be one for anything that is “real” and can be measured. You will learn many of them, and we will give them a generic symbol: $\widehat{\mathit{\Omega}}$, where the “hat” signifies a quantum mechanical operator. We will use the $\mathit{\Phi}$ symbol for the wave equation that $\widehat{\mathit{\Omega}}$ operates on (and unfortunately $\mathit{\Phi}$ are also called eigenfunctions, because people like to give names to things that already have names). You may also have noticed that when we applied the kinetic energy operator: $\widehat{\mathit{\Omega}} = frac{-}\hbar^2 2m\frac{\partial^2}{\partial x^2}$ to the wave equation:$mathit\Phi = cos\left(\frac{2\pi}{\lambda}x\right)$ that we were able to calculate the energy via what is called the “eigenvalue equation”:

$$\widehat{\mathit{\Omega}}\mathit{\Phi} = \omega\mathit{\Phi}$$

where “ω” is the result of the eigenvalue equation and is creatively called the eigenvalue. For instance, application of the kinetic energy operator returned an eigenvalue ω, which happened to be the kinetic energy. Quite useful if you want to know the kinetic energy.

Eigen is German for “same”, which refers to the fact that the wave equation $\mathit{\Phi}$ appears to the left and right side of the eigenvalue equation. This reveals an absolutely crucial aspect of quantum mechanics, which is that ***if the wave equation doesn’t appear exactly as is on both the left and right, then the eigenvalue is meaningless***. For example, if we have an operator $\widehat{\mathit{\Omega}}$ that acts on $\mathit{\Phi} = N \cdot cos\left(\frac{2\pi}{\lambda}x\right)$ as follows:

$$\widehat{\mathit{\Omega}}\mathit{\Phi} = \widehat{\mathit{\Omega}}\,cos\left(\frac{2\pi}{\lambda}x\right) = \frac{2\pi}{\lambda} \cdot sin\left(\frac{2\pi}{\lambda}x\right) \neq \omega\mathit{\Phi} or \widehat{\mathit{\Omega}}\mathit{\Phi} = \widehat{\mathit{\Omega}}\,cos\left(\frac{2\pi}{\lambda}x\right) = x \cdot cos\left(\frac{2\pi}{\lambda}x\right) \neq \omega\mathit{\Phi}$$

then these examples are quantum mechanical “fails”, and nothing can be learned from the results. If the wave equation appears exactly the same on left and right side, then we say that the wave equation $\mathit{\Phi}$ is an eigenfunction of the operator $\widehat{\mathit{\Omega}}$. To verify our understanding, we will measure the kinetic energy once again:

$$\widehat{\mathit{\Omega}}\mathit{\Phi} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\,cos\left(\frac{2\pi}{\lambda}x\right)\omega\mathit{\Phi} = \frac{2\pi^2\hbar^2}{m\lambda^2}cos\left(\frac{2\pi}{\lambda}x\right) = \omega\mathit{\Phi}$$

”This is a good example, and we know that the kinetic energy of the particle that is described by the wave equation $\mathit{\Phi} = cos\left(\frac{2\pi}{\lambda}x\right)$ is: $\frac{2\pi^2\hbar^2}{m\lambda^2}$. The wave equation(s) that work with an operator are often referred to as “belonging” to that operator; the proper way of saying this is to state, “the set of one or more functions $\mathit{\Phi}$ are eigenfunctions of the operator $\widehat{\mathit{\Omega}}$”.

As we move forward you will learn many more operators. Some of them are very special, such as the Hamiltonian operator that returns the total energy. The Hamiltonian is given the symbol $\hat{H}$; likewise, the wave equations of the Hamiltonian are called “wavefunctions” and are given the symbol ψ. Thus, the eigenvalue equation for the Hamiltonian is properly expressed as: $\hat{H}\psi = E\psi$, where we also changed the symbol for the eigenvalue (ω) to “E” for energy. Recall that you have already seen the Hamiltonian operator

$$\hat{H} = \frac{-\hbar^2}{2m}\nabla^2 + \hat{V}$$

where $\hat{V}$ is the potential energy operator, which is usually a function of position. We believe the wavefunctions ψ of the Hamiltonian operator are the most meaningful results of quantum mechanics because we believe that they are “real”. In fact, all the learnings you have had previously about atomic structure, such as s- and p-orbitals of hydrogen and heavier elements, are in fact wavefunctions of the atom’s Hamiltonian.

Let’s see a few more operators. Given that particles have momentum, and that is something we can definitely measure, there must be an associated quantum mechanical operator for it. In fact, the momentum operator ($\hat{p}$) is:

$$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

This is fully consistent with our kinetic energy operator $\frac{\hat{p}^2}{2m}$ as follows:

$$\frac{\hat{p}\hat{p}}{2m} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{1}{2m}\frac{\hbar^2}{i^2}\frac{\partial^2}{\partial x^2} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Another operator is the position operator $\hat{x}$, which is quite simple: $\hat{x} = x$. More complex operators include the z-component of angular momentum $\widehat{j_z} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$, which we will cover in a later chapter. The important thing to know is that there are many operators for calculating many different properties from quantum mechanical objects such as electrons and molecules.

12.4.1 Eigenfunctions of different operators

There is one last, very important lesson about operators and eigenfunctions which is one of the most complicated things about quantum mechanics. And that is the fact that the eigenfunctions of one operator may, ***or may not***, be the eigenfunctions of another operator. This is shown by the Venn diagram in Figure 12.4, and as an example let’s go back to the example of a Hamiltonian operator with no potential energy, i.e. $\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. A wavefunction of this Hamiltonian is $\psi = cos\left(\frac{2\pi}{\lambda}x\right)$, and has an energy as we showed on the previous page. Now, if we apply the momentum operator to the same state:

$$\hat{p}\psi = \frac{\hbar}{i}\frac{\partial}{\partial x}cos\left(\frac{2\pi}{\lambda}x\right) = \frac{-2\pi\hbar}{i\lambda} \cdot sin\left(\frac{2\pi}{\lambda}x\right) \neq \omega\psi$$

Then you should know that the momentum of the state ***most definitely is not*** $\frac{-2\pi\hbar}{i\lambda}$. The next section will discuss in great detail how we deal with this uncomfortable situation.

12.4.2 Practice with the Eigenvalue Equation and Complex Wave Equations.

We have already shown that wave equations, when squared, provides a measure of probability that a quantum mechanical particle is at a particular position. We have also shown how a wave equation can provide additional information, that being what is returned when it is operated on by, oddly, operators. We will make this more concrete with examples here. Let’s say that the normalized wavefunction for an electron is: $\psi = N \cdot cos(kx)$ where N is the normalization constant and $k = \frac{2\pi}{\lambda}$ is the wavevector. We know how to square this function, which then tells us the probability that the electron is at a position x that we are curious about (for whatever reason). What about the energy of this electron? Just like in the previous examples we apply the potential energy free (i.e. $\hat{V} = 0$) Hamiltonian:

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\{N \cdot cos(kx)\} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\{N \cdot k \cdot sin(kx)\} = \frac{\hbar^2 k^2}{2m}\{N \cdot cos(kx)\}$$

Comparison to the eigenvalue equation $\hat{H}\psi = E\psi$ reveals that the above is in the proper form, so we can be sure that the energy is: $\frac{\hbar^2 k^2}{2m}$.

Now let’s repeat the above using the complex mathematical version of the wavefunction, i.e. $\psi = N \cdot cos(kx) = N \cdot \left(\frac{1}{2}e^{ikx} + \frac{1}{2}e^{-ikx}\right)$:

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\{N \cdot \left(\frac{1}{2}e^{ikx} + \frac{1}{2}e^{-ikx}\right)\right\} = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left\{N \cdot \left(\frac{ik}{2}e^{ikx} + \frac{-ik}{2}e^{-ikx}\right)\right\} =$$

$$-\frac{\hbar^2}{2m}\left\{N \cdot \left(\frac{-k^2}{2}e^{ikx} + \frac{-k^2}{2}e^{-ikx}\right)\right\}$$

The next step is to factor out $-k^2$ which gives us:

$$\hat{H}\psi=\frac{\hbar^2k^2}{2m}\left\{N\cdot\left(\frac{1}{2}e^{ikx}+\frac{1}{2}e^{-ikx}\right)\right\}=E\psi$$

where again we see that $E=\frac{\hbar^2k^2}{2m}$. So, everything seems fine, but why are we using this approach? While solving $\hat{H}\psi$ using the complex representation of $\psi=N\cdot cos\left(kx\right)$ seems more difficult, there are going to be many examples coming up where the complex representation is far easier to work with. For example, the electron's wavefunction could have been $\psi=N\cdot e^{ikx}$. In this case, which do you think is harder to solve:

$$\hat{H}\psi=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\{N\cdot e^{ikx}\right\}$$

or:

$$\hat{H}\psi=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\{N\cdot cos\left(kx\right)+i\cdot sin\left(kx\right)\right\}$$

Just for the heck of it let's solve the former:

$$\hat{H}\psi=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left\{N\cdot e^{ikx}\right\}=-\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left\{ik\cdot N\cdot e^{ikx}\right\}=-\frac{\hbar^2}{2m}\left\{i^2k^2\cdot N\cdot e^{ikx}\right\}=\frac{\hbar^2k^2}{2m}\left\{N\cdot e^{ikx}\right\}$$

Taking the derivative of an exponential is easy, and just like the previous example, we see that $E=\frac{\hbar^2k^2}{2m}$. This wasn't nearly as hard as taking the double derivative of two trig functions!

12.4.2.1Applications of other operators.

Let's continue to work with $\psi=N\cdot e^{ikx}$, from which we will extract the momentum via $\hat{p}$:

$$\hat{p}\psi=\frac{\hbar}{i}\frac{\partial}{\partial x}\left\{N\cdot e^{ikx}\right\}=\frac{\hbar}{i}\left\{ik\cdot N\cdot e^{ikx}\right\}=\hbar k\left\{N\cdot e^{ikx}\right\}$$

Here we get a "pass" on the eigenvalue equation $\widehat{\Omega}\Phi=\omega\cdot\Phi$ because the wavefunction is present on both the right and left sides. Therefore, we do know that the momentum of a particle with this wavefunction is $p=\hbar k$ and it has an energy of $E=\frac{\hbar^2k^2}{2m}$. Notice the consistency, as in the absence of potential the total energy is $E=\frac{p^2}{2m}$, and inserting p=$hslashk$ yields $E=\frac{\hbar^2k^2}{2m}$. If the wavefunction of the electron was $\psi=N\cdot e^{-ikx}$, we would have still found $\frac{\hbar^2k^2}{2m}$ of energy but $-\hbar k$ of momentum (note that this is still consistent with $E=\frac{p^2}{2m}$). Why would one wavefunction have a positive momentum and the other negative? Why, the interpretation is simple, $\psi=N\cdot e^{ikx}$ represents a particle moving forward and $\psi=N\cdot e^{-ikx}$ is moving backwards!

Now let's double check our math abilities one last time with $\psi=N\cdot cos\left(kx\right)$, from which we will calculate the momentum.

$$\hat{p}\psi=\frac{\hbar}{i}\frac{\partial}{\partial x}\left\{N\cdot cos\left(kx\right)\right\}=\frac{-\hbar k}{i}\left\{N\cdot sin\left(kx\right)\right\}=i\hbar k\left\{N\cdot sin\left(kx\right)\right\}$$

where we used the identity $\frac{-1}{i}=i$ in the last step. Now we ask, is this electron moving to the right with an imaginary amount of momentum? What does it mean for this electron to have imaginary momentum? Why, it means absolutely nothing- there is no such thing as imaginary momentum, which should be a clue that you screwed up the question. What did you do wrong? You didn't get the correct eigenvalue equation $\widehat{\Omega}\Phi=\omega\cdot\Phi$ as you don't have the wavefunction on the left- and right-hand side equal to each other:

$$\hat{p}\left\{N\cdot cos\left(kx\right)\right\}\neq\hat{p}\left\{N\cdot sin\left(kx\right)\right\}$$

After all, cosine and sine are not the same thing.

As discussed in the previous section, the eigenfunctions of one operator may, or may not, be the eigenfunctions of another operator. Here, the wavefunctions $\psi=N\cdot e^{ikx}, N\cdot e^{-ikx}$, and \(N\cdot cos(kx))are all "good" with the Hamiltonian because they all deliver on $\hat{H}\psi=E\psi$. However, only $\psi=N\cdot e^{ikx}$ and $N\cdot e^{-ikx}$ are eigenfunctions of the momentum operator, but $\psi=N\cdot cos(kx)$ is not. Does this seem messy? It should, and it is, which is why we have to have multiple classes to discuss quantum mechanics.

12.4.2 Expectation Values

How do we figure out the momentum of a particle with a wavefunction of the form$psi=N\cdot cos(kx)$? Give up? Sometimes! After all quantum mechanics is all about probability, and you cannot know everything. In this case, instead of giving up you can often solve these types of problems using the following approach. If we write out:

\[\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)\ =\frac{N}{2}e^{ikx}+\frac{N}{2}e^{-ikx} \nonumber \]

you notice that particle's wavefunction is composed of two equal momentum eigenfunctions, one that is moving to the right (e^{ikx}) and the other to the left (e^{-ikx}). Now you can guess that the total momentum is 0. Good intuition, but quantum class is sort of a math class, so how do we prove it? Here we introduce a new expression that is called the "expectation value" for an operator $\widehat{\Omega}$:

$$\langle\widehat{\Omega}\rangle=\int_{lower\ limit}^{upper\ limit}\psi^*\widehat{\Omega}\psi\cdot\partial\tau$$

where ψ may, or may not, be the eigenfunction of the operator $\widehat{\Omega}$. What is great about expectation values is that it doesn't matter- in either case you will get the right answer. Let's apply this to our current problem with determining the momentum of \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)):

\[\langle \hat{p}\rangle =\int^{upper\ limit}_{lower\ limit}{}{\left\{N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)right\}}^*\frac\hslash{i}\frac{\partial }{\partial x}\left\{N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)right\}\cdot \partial x \nonumber \]

\[\frac{-\hslash }{i}N^2\int^{\infty }_{-\infty }{}

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(kx\right)cdot \partial x \nonumber \]

When we look up this integral off the internet, we find \(\int^{\infty }_{-\infty }{}

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(kx\right)cdot \partial x=0\). So, as we can see $\langle\hat{p}\rangle=0$, in other words this quantum object has no net momentum. This is in fact the correct answer. While this problem is a bit difficult, notice how we were able to determine the momentum with this approach whereas the eigenvalue equation proved useless. So, we have that going for us, which is nice.

The expectation value approach also works with functions that are eigenfunctions. Let's do an example using the normalized "right wave" $\varPhi=N\cdot e^{ikx}$ eigenfunction of momentum, that being the:

$$\langle\hat{p}\rangle=\int_{lower\,limit}^{upper\,limit}\left\{N\cdot e^{ikx}\right\}^{*}\frac{\hbar}{i}\frac{\partial}{\partial x}\left\{N\cdot e^{ikx}\right\}\cdot\partial x=$$

$$\langle\hat{p}\rangle=\frac{\hbar}{i}\int_{-\infty}^{\infty}N^{*}\cdot e^{-ikx}\cdot ik\cdot N\cdot e^{ikx}\cdot\partial x=$$

$$\langle\hat{p}\rangle=\frac{\hbar ik}{i}\int_{-\infty}^{\infty}N^{*}\cdot e^{-ikx}\cdot N\cdot e^{ikx}\cdot\partial x=\hbar k\int_{-\infty}^{\infty}\varPhi^{*}\varPhi\cdot\partial x=\hbar k$$

where the complex conjugate $\left\{N\cdot e^{ikx}\right\}^{*}$ is: $N^{*}\cdot e^{-ikx}$, and we used the formula $\int\varPhi^{*}\varPhi\partial x=\int|\varPhi|^{2}\partial x=1$ in the last step which is the definition of normalization. While we determined the corrent momentum, you might ask, why not stick with $\widehat{\varOmega}\varPhi=\omega\cdot\varPhi$ given that $\langle\hat{p}\rangle$ was seemingly much more complicated to work with? You are correct, it is generally mathematically far simpler to work with the eigenvalue equation over the expectation value expression. However, the expectation value method always works, and also gives us a "clean" answer because we don't have to try to untangle the eigenvalue from the eigenfunction.

Now you might ask, why does the expectation value method work? For one, if we are working on eigenfunctions of the operator $\widehat{\varOmega}$, the answer is seen in a simple derivation:

$$\langle\widehat{\varOmega}\rangle=\int_{-\infty}^{\infty}\varPhi^{*}\widehat{\varOmega}\varPhi\cdot\partial\tau=\int_{-\infty}^{\infty}\varPhi^{*}\cdot\omega\cdot\varPhi\cdot\partial\tau=\omega\cdot\int_{-\infty}^{\infty}\varPhi^{*}\cdot\varPhi\cdot\partial\tau=\omega$$

where we assume that $\varPhi$ is normalized. However, this proof breaks down when we are not applying an eigenfunction of the operator, i.e. when $\widehat{\varOmega}\psi\neq\omega\cdot\psi$. What do we do in this case? Here is another important lesson, which is that wavefunctions can always be written as linear combinations of other wavefunctions. For example, let's say that the operator $\widehat{\varOmega}$ has two eigenfunctions $\varPhi_1$ and $\varPhi_2$, but ψ is not an eigenfunction of $\widehat{\varOmega}$. Upon further analysis you realize that ψ is a linear combination of the $\varPhi's$:

$$\psi=c_1\cdot\varPhi_1+c_2\cdot\varPhi_2$$

where c_1 and c_2 are constants. When you apply the above to the expectation value expression:

$$\langle\widehat{\varOmega}\rangle=\int_{-\infty}^{\infty}\psi^{*}\widehat{\varOmega}\psi\cdot\partial\tau=\int_{-\infty}^{\infty}\left\{c_1\cdot\varPhi_1+c_2\cdot\varPhi_2\right\}^{*}\widehat{\varOmega}\left\{c_1\cdot\varPhi_1+c_2\cdot\varPhi_2\right\}\cdot\partial\tau$$

This problem has now turned into an algebraic mess which is a common occurrence. Fortunately, algebra is a middle school level of mathematics and as such we can deal with it:

$$\langle\widehat{\varOmega}\rangle=\int_{-\infty}^{\infty}\left\{c_1\cdot\varPhi_1+c_2\cdot\varPhi_2\right\}^{*}\widehat{\varOmega}\left\{c_1\cdot\varPhi_1+c_2\cdot\varPhi_2\right\}\cdot\partial\tau=$$

$$\int_{-\infty}^{\infty}\left\{c_1^{*}\varPhi_1^{*}\widehat{\varOmega}c_1\varPhi_1+c_2^{*}\varPhi_2^{*}\widehat{\varOmega}c_2\varPhi_2+c_1^{*}\varPhi_1^{*}\widehat{\varOmega}c_2\varPhi_2+c_2^{*}\varPhi_2^{*}\widehat{\varOmega}c_1\varPhi_1\right\}\cdot\partial\tau$$

This can be broken up into four smaller integrals which is less scary.

$$\langle\widehat{\varOmega}\rangle=\int_{-\infty}^{\infty}c_1^{*}\varPhi_1^{*}\widehat{\varOmega}c_1\varPhi_1\cdot\partial\tau+\int_{-\infty}^{\infty}c_2^{*}\varPhi_2^{*}\widehat{\varOmega}c_2\varPhi_2\cdot\partial\tau+\int_{-\infty}^{\infty}c_1^{*}\varPhi_1^{*}\widehat{\varOmega}c_2\varPhi_2\cdot\partial\tau+\int_{-\infty}^{\infty}c_2^{*}\varPhi_2^{*}\widehat{\varOmega}c_1\varPhi_1\cdot\partial\tau$$

We can simplify this further using the relationships:

$$\widehat{\varOmega}c_1\varPhi_1=\omega_1\cdot c_1\varPhi_1,\widehat{\varOmega}c_2\varPhi_2=\omega_2\cdot c_2\varPhi_2,c_1^{*}c_1=|c_1|^{2},and c_2^{*}c_2=|c_2|^{2}$$

to yield:

$$\langle\widehat{\varOmega}\rangle=|c_1|^{2}\cdot\omega_1\cdot\int_{-\infty}^{\infty}|\varPhi_1|^{2}\cdot\partial\tau+|c_2|^{2}\cdot\omega_2\cdot\int_{-\infty}^{\infty}|\varPhi_2|^{2}\cdot\partial\tau+c_1^{*}c_2\cdot\omega_2\int_{-\infty}^{\infty}\varPhi_1^{*}\varPhi_2\cdot\partial\tau+c_2^{*}c_1\cdot\omega_1\int_{-\infty}^{\infty}\varPhi_2^{*}\varPhi_1\cdot\partial\tau$$

Now the above monster can be solved using something that we know already, which is that eigenfunctions are normalized:

$$\int_{-\infty}^{\infty}|\varPhi_1|^{2}\cdot\partial\tau=\int_{-\infty}^{\infty}|\varPhi_2|^{2}\cdot\partial\tau=1$$

Now we also must introduce a new concept called "orthonormality" for the 3^{rd} and 4^{th} expression above:

$$\int_{-\infty}^{\infty}\varPhi_1^{*}\varPhi_2\cdot\partial\tau=\int_{-\infty}^{\infty}\varPhi_2^{*}\varPhi_1\cdot\partial\tau=0$$

What this means is that, for two eigenfunctions of the same operator, when you integrate them together you get 0. The proper language is that "they do not overlap", and we will explain this further in the next section on Hermitian operators. Regardless, the remainder of the proof is:

$$\langle\widehat{\varOmega}\rangle=|c_1|^{2}\cdot\omega_1+|c_2|^{2}\cdot\omega_2$$

Now you may have said to yourself, "I can't imagine when would I every run into an equation like: $\psi=c_1\cdot\varPhi_1+c_2\cdot\varPhi_2$." Actually, you already have, with:

\[N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)\ =\frac{N}{2}e^{ikx}+\frac{N}{2}e^{-ikx} \nonumber \]

Here, \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)), $c_1=\frac{1}{2}$ and $c_2=\frac{1}{2}$ and $\mathit{\Phi}_1=e^{ikx}$ and $\mathit{\Phi}_2=e^{-ikx}$. We have already shown that ψ is not the eigenfunction of the momentum operator $\hat{p}$, although $\mathit{\Phi}_1$ and $\mathit{\Phi}_2$ are since $\hat{p}\,\mathit{\Phi}_1=\hbar k\cdot\mathit{\Phi}_1$ and $\hat{p}\,\mathit{\Phi}_2=-\hbar k\cdot\mathit{\Phi}_2$. Since ψ can be expressed as a linear combination of that are eigenfunctions of $\hat{p}$ we can plug all this information into $\langle\hat{p}\rangle=|c_1|^2\cdot\omega_1+|c_2|^2\cdot\omega_2$ to find:

$$\langle\hat{p}\rangle=\left|\frac{1}{2}\right|^2\cdot\hbar k+\left|\frac{1}{2}\right|^2\cdot(-\hbar k)=0$$

Consequently, we not only see once again how the expectation value can allow us to figure out observables from difficult functions (ones that are not eigenfunctions), we also see how it works. We also see that \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)) describes a particle that isn’t moving. \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(kx\right)) would do the same thing.

12.4.3 Schrödinger’s Cat

In the previous example, it was found that a quantum particle described by the wavefunction $\psi=N\cdot cos\left(kx\right)$ or $\psi=N\cdot sin\left(kx\right)$ have $\langle\hat{p}\rangle=0$. However, does this mean that $E=\frac{p^2}{2m}=0$? Afterall, this is a particle with no potential energy. And now we ””””””””””have a conundrum because we already demonstrated that $E=\frac{p^2}{2m}=\frac{\hbar^2k^2}{2m}$! The resolution lies in the fact that these trigonometric wavefunctions are composed of equal left- and right-travelling waves. Meaning that the particle has momentum, and thus kinetic energy, but since the momentum can be pointed either left or right they cancel each other out to yield a net $\langle\hat{p}\rangle=0$! This is an example of quantum superposition, as exemplified by the famous Schrödinger’s cat who is both alive and dead at the same time as explained in the box. It is important to note that the superposition is not because the particle is moving right and left at the same time, rather, the wavefunction is used because the experimentalist was not able (or wasn’t told) about which direction the particle is travelling. Although it is true that the particle is moving either right or left, and an experimentalist was able to guess which direction and use the corresponding wavefunction for further analysis, the results would turn out to be incorrect. This seems like absolute nonsense, but this is true and has been confirmed multiple times. In fact, quantum superposition is the basis for quantum computing.

12.4.4 Expectation Value examples: Position

We have already discussed how the position operator $\hat{x}$ is simply x. Consequently, let’s apply the operator to our favorite wavefunction \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)), and recall for the eigenvalue equation to work properly (for ψ to be an eigenfunction of $\widehat{\mathit{\Omega}}$) we need to see that $\widehat{\mathit{\Omega}}\psi=\omega\cdot\psi$:

\[\hat{x}\psi =x\cdot N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)\ \nonumber \]

Whups- this is a fail, the wavefunction on the right is supposed to be a number (ω) multiplying the original wavefunction. However, if \(\left(kx\right)) and \(\left(kx\right)), then clearly $f(x)\neq g(x)$ since “x” is not a finite value like 5 or \piup. To be more plainspoken, you need to see $\omega=5$ or $\omega=\pi$, not $\omega=x$. The example above is undoubtedly confusing; we have two explanations. For one, the application of an operator is akin to asking a question. The position operator is asking, “Where are you at?” However, this question is nonsensical when applied to \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)), since technically this wave is somewhere everywhere from -∞ to ∞. Thus, the question itself is not sensible, and thus there is an uninterpretable result. Another, easier explanation is that ψ is not an eigenfunction of $\hat{x}$. And in these cases you need to apply the expectation value way of answering quantum mechanical questions. If you’re interested in what is an eigenfunction of x, look up “Dirac Delta Functions”.

12.4.5 Hermitian operators

One of the most important relationships in quantum mechanics is called orthonormality. This means that, if you have a few functions ψ_n that are eigenfunctions of the operator $\widehat{\mathit{\Omega}}$, then the following is true:

`\int^{upper\ limit}_{lower\ limit}{}{{\psi }^*_{n^'}\psi }_n\cdot \partial \tau ={\delta }_{n^',n} \nonumber`

Where d is the Kronecker delta function:

`{\delta }_{n^',n}={\{}^{1,\ if\ n^'=n\ }_{0,\ if\ n^'\neq n} \nonumber`

We saw this previously in our discussion on the proof of the expectation value equation. Where does this come from? It is assumed that the wavefunctions are eigenfunctions of an operator that is Hermitian. The definition of a Hermitian operator is:

`\int{}{\psi }^*_{n^'}\widehat{\mathit{\Omega}}{\psi }_n\cdot \partial \tau =\int{}{\psi }_n{\left({\widehat{\mathit{\Omega}}\psi }_{n^'}\right)}^*\cdot \partial \tau \nonumber`

Now while this seems very abstract, you’re right, it is. However, it turns out that nearly all quantum mechanical operators (and most important the Hamiltonian operator) has this mathematical trait. The fact that the operator behaves this way has implications for the solutions to the operator, i.e. the wavefunctions. To see what we mean, first assume that the wavefunctions ψ_n and `{\psi }_{n^'}` are actually the exact same thing, meaning `n=n^'`. Also $\widehat{\mathit{\Omega}}\psi_n=\omega_n\psi_n$. As a result:

$$\int \psi_n^* \widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_n^* \omega_n \psi_n \cdot \partial\tau = \omega_n \cdot \int \psi_n^* \psi_n \cdot \partial\tau$$

Also:

$$\int \psi_n \left(\widehat{\Omega}\psi_n\right)^* \cdot \partial\tau = \int \psi_n (\omega_n \psi_n)^* \cdot \partial\tau = \omega_n^* \cdot \int \psi_n \psi_n^* \cdot \partial\tau$$

Since, for a Hermitian operator $\int \psi_n^* \widehat{\Omega}\psi_n \cdot \partial\tau = \int \psi_n \left(\widehat{\Omega}\psi_n\right)^* \cdot \partial\tau$, then:

$$\omega_n \cdot \int \psi_n^* \psi_n \cdot \partial\tau = \omega_n^* \cdot \int \psi_n \psi_n^* \cdot \partial\tau$$

And thus:

$$\omega_n \cdot \int \psi_n^* \psi_n \cdot \partial\tau - \omega_n^* \cdot \int \psi_n \psi_n^* \cdot \partial\tau = (\omega_n - \omega_n^*) \int \psi_n^* \psi_n \cdot \partial\tau = 0$$

Where we used the fact that, through the associative axiom of multiplication: $\int \psi_n^* \psi_n \cdot \partial\tau = \int \psi_n \psi_n^* \cdot \partial\tau$. Now, there are only two ways for $(\omega_n - \omega_n^*) \int \psi_n^* \psi_n \cdot \partial\tau = 0$, either $\int \psi_n^* \psi_n \cdot \partial\tau = 0$ which we already know is false (its equal to 1) or $\omega_n - \omega_n^* = 0$, which means that $\omega_n = \omega_n^*$. When is a number equal to its complex conjugate? Only when that number is fully real. Thus, the eigenvalues of Hermitian operators have real eigenvalues.

Next assume that `n\neq n^'`. The same analyses above yield:

`\int{}{\psi }^*_{n^'}\widehat{\mathit{\Omega}}{\psi }_n\cdot \partial \tau =\int{}{\psi }^*_{n^'}{\omega }_n{\psi }_n\cdot \partial \tau ={\omega }_n\cdot \int{}{\psi }^*_{n^'}{\psi }_n\cdot \partial \tau \nonumber`

Also:

`\int{}{\psi }_n{\left({\widehat{\mathit{\Omega}}\psi }_{n^'}\right)}^*\cdot \partial \tau =\int{}{\psi }_n{\left({\omega }_{n^'}{\psi }_{n^'}\right)}^*\cdot \partial \tau ={\omega }^*_{n^'}\cdot \int{}{\psi }_n{\psi }^*_{`

Since `\int{}{\psi }^*_{n^'}\widehat{\mathit{\Omega}}{\psi }_n\cdot \partial \tau =\int{}{\psi }_n{\left({\widehat{\mathit{\Omega}}\psi }_{n^'}\right)}^*\cdot \partial \tau` then:

`\left({\omega }_n-{\omega }^*_{n^'}\right)\int{}{\psi }^*_{n^'}{\psi }_n\cdot \partial \tau =0 \nonumber`

And we now have to figure out whether `{\omega }_n-{\omega }^*_{n^'}=0` or if `\int{}{\psi }^*_{n^'}{\psi }_n\cdot \partial \tau =0`. Now, if ψ_n and `{\psi }_{n^'}` are different eigenfunctions of the operator then they must have different eigenvalues. If not, they would be the same. Thus, `{\omega }_n\neq {\omega }_{n^'}`, and we have to conclude that different eigenfunctions of the same operator are orthonormal:

`\int{}{\psi }^*_{n^'}{\psi }_n\cdot \partial \tau ={\{}^{1,\ if\ n^'=n\ }_{0,\ if\ n^'\neq n} \nonumber`

12.5: The Freewave Potential

In the next few sections we will examine a few paradigms of systems that are good first examples. The first is called the “free wave” particle, which is a quantum mechanical object (let’s just say its an electron), that lives in a single dimension without end. Also, there is nothing to interact with. As a result, the Hamiltonian: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V\left(x\right)$ of that particle is simply:

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

since V(x)=0 everywhere (no potential for interaction because there is nothing else to interact with). While this is a simple problem to work with, it has the unfortunate aspect of being highly unrealistic for describing the Universe with only one particle, and that the Universe doesn’t end (fyi ours does, thanks to the Big Bang).

You may have already figured out that we have been working with the free wave system for this entire chapter. As a result we already know that there are four wavefunctions, and that $\psi=N\cdot e^{ikx}$ is for a particle moving right, $\psi=N\cdot e^{-ikx}$ is for a particle moving left, and \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(kx\right)) and \(\psi =N\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(kx\right)) are for particles that have no net momenta. Great, but here is something you may have not noticed. Let’s normalize the wavefunction by deriving the normalization constant that we already discussed is:

$$N=\frac{1}{\sqrt{\int\psi^2\partial\tau}}$$

And let’s use an unnormalized wavefunction $\psi=e^{ikx}$ (recall, that our purpose here is to calculate what “N” is). First let’s simply solve the integral

$$\int_{-\infty}^{\infty}\psi^2\cdot\partial x=\int_{-\infty}^{\infty}\psi^*\psi\cdot\partial x=\int_{-\infty}^{\infty}e^{ikx*}e^{ikx}\cdot\partial x=\int_{-\infty}^{\infty}e^{-ikx}e^{ikx}\cdot\partial x=\int_{-\infty}^{\infty}\partial x=\infty$$

To solve this we used the fact that $e^{-ikx}e^{ikx}=e^{-ikx+ikx}=e^0=1$. Thus, the normalized wavefunction is: $\psi=N\cdot e^{ikx}=\frac{1}{\sqrt{\infty}}e^{ikx}$. In case you are wondering, no this doesn’t make sense. You can’t have equations with ∞ in it, and the square root doesn’t “save” it in some miraculous way. This normalized wavefunction is absurd, so you may be wondering how you fix it.

The answer is, you don’t. You see, the problem itself is absurd, because this is a particle that is in an infinite universe and the particle may be found anywhere in it. Thus, the probability density for the normalized wavefunction $\psi^*\psi$ is:

$$\psi^*\psi=\frac{1}{\sqrt{\infty}}e^{-ikx}\frac{1}{\sqrt{\infty}}e^{ikx}=\frac{1}{\infty}=0$$

And this is exactly what you should get. In an infinite universe, the probability for a particle to be at any particular point in space is 0 because the particle has an infinite number of other places to be. So, the result is fine, just weird.

Example problems, the “particle in a box”. This paradigm is a bit more simple, which is that the free wave is in fact inside a finite universe. Inside the box there is no potential energy, so $\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. Outside the boundaries the potential energy is infinite, so the particle cannot leave the box. To make it interesting, we often make the particle have the mass of an electron and the box is 1×10^{-9} m (or 1 nm) big, which means that the electron displays quantum mechanical behavior. If the box was much bigger then the electron is just like a marble on a track, and we don’t really need quantum mechanics to describe it. This is a lesson that there are size regimes over which you observe quantum mechanical effects, and bigger ones where you don’t.

Shown on the right is the potential surface. Since the wavefunction $\psi\left(x\right)$ has to be$psi\left(0\right)=0$ at x=0, and$psi\left(L\right)=0$ at x=L, and have a double derivative that is equal to itself, the only mathematical entity that fits the bill for is $\psi=N\cdot sin(?)$. Now, we must design the argument of the function “?” to sure that \(

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(x=L\right)\ =0\). A sine wave always starts at 0, and it next crosses 0 at \piup. Thus, we know that:

$$\psi\left(x\right)=\left(\pi\frac{x}{L}\right)$$

works. Now, you might recall that we often found more than one solution to a problem; the free wave has four solutions for example. As you can see from the figure, the particle in a box also has more solutions because the sine wave has other 0’s, the first one at p and the next one at 2p. Thus, another solution to the particle in a box is \(\psi \left(x\right)=N\cdot

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(2\pi \frac{x}{L}\right)). And we can keep figuring out new solutions until we see that there is a general relationship \(\left(n\pi \frac{x}{L}\right)), where n=1, 2, 3…

While we have an infinite number of solutions for the particle in a box problem, how do we understand what they mean or represent? First, let’s figure out how to normalize them. As we have already shown many times that the normalization constant is $N=\frac{1}{\sqrt{\int\psi^2\partial\tau}}$, let’s simply calculate the integral:

$$\int_0^L\psi^2\cdot\partial x=\int_0^L\psi^*\psi\cdot\partial x=\int_0^L sin\left(n\pi\frac{x}{L}\right)^*sin\left(n\pi\frac{x}{L}\right)\cdot\partial x=\int_0^L sin^2\left(n\pi\frac{x}{L}\right)\cdot\partial x$$

To solve this we simply look up a table of standard trigonometric integrals to find:

$$\int(ax)\,partialx=\frac{x}{2}-\frac{1}{4a}sin(2ax)$$

and thus: $\int\left(n\pi\frac{x}{L}\right)partialx=\frac{x}{2}-\frac{L}{4n\pi}sin(2n\pi\frac{x}{L})$. When placed into a definite integral:

\[\int^L_0{}{sin}^2\left(n\pi \frac{x}{L}\right)\cdot \partial x={\frac{x}{2}-\frac{L}{4n\pi }sin(2n\pi \frac{x}{L})]}^{x=L}_{x=0}=\frac{L}{2}-\frac{L}{4n\pi }

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(2n\pi \right)\ =\frac{L}{2} \nonumber \]

because \(

▯ UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(2n\pi \right)\ =0\) since n is a whole number integer, i.e. since n=1, 2, 3… then \(

▯ UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(2n\pi \right)\ =

▯ UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(4\pi \right)=

▯ UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(6\pi \right)\ =0).

As a result, the proper normalized particle in a box wavefunctions are:

$$\left(n\pi\frac{x}{L}\right)$$

Now for their interpretation, first we can calculate the energy. We will use the eigenvalue expression $\hat{H}\psi_n(x) = E\cdot\psi_n(x)$ since this is usually the fastest way if you know you are dealing with the eigenfunctions of the operator (here, the Hamiltonian).

$$\hat{H}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(n\pi\frac{x}{L}\right) \quad = \frac{n^2\pi^2}{2mL^2}\left(n\pi\frac{x}{L}\right)$$

As a result we see that the energy is $E_n = \frac{n^2\pi^2}{2mL^2}$. Since n=1, 2, 3… then the n=1 state is the ground state and all the others are excited states, as these have higher energies than the ground state.

We can also figure out the average position of the particle in a box via the expectation value, which is always necessary when using the operator. Note that you must use normalized wavefunctions to properly evaluate expectation values.

\langle \hat{x}\rangle =\int^{upper}_{lower}{}{\psi }^*_{n^'}{\hat{x}\psi }_n\cdot \partial \tau =\int^L_0{}{\left(\left(n\pi \frac{x}{L}\right)right)}^*\cdot x\cdot \left(n\pi \frac{x}{L}\right)cdot \partial x \nonumber

Of course we know that sine functions are not complex, so $sin(x)^* = sin(x)$, and we can do some factoring to simplify the above into:

$$\langle\hat{x}\rangle = \frac{2}{L}\int_0^L x\cdot\left(n\pi\frac{x}{L}\right) cdot\partial x$$

Use of a table of trigonometric identities yields:

\langle \hat{x}\rangle =\frac{2}{L}\int{}x\cdot \left(n\pi \frac{x}{L}\right)cdot \partial x=\frac{2}{L}\left\{{\frac{x^2}{2}-\frac{xL}{4n\pi }{{sin}}sinleft(2n\pi \frac{x}{L}\right)\ -\frac{x^2}{4}-\frac{L^2}{8n^2{\pi }/

Inputting the limits and using the normalizer gives:

\[\langle \hat{x}\rangle =L-\frac{L}{2n\pi }

▯ UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(2n\pi \right)\ -\frac{L}{2}-\frac{L}{4n^2{\pi }^2}

▯ UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(2n\pi \right)\ +\frac{L}{4n^2{\pi }^2} \nonumber \]

Since \(

▯ UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(2n\pi \right)) and \(

▯ UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(2n\pi \right)) are always 0 and 1, respectively, for n=1, 2, 3… then we are left with:

$$\langle\hat{x}\rangle = L - \frac{L}{2} = \frac{L}{2}$$

And thus $\langle\hat{x}\rangle = \frac{L}{2}$, the middle of the box, for every state of the particle in the box since there is no dependence on the quantum number n in the equation above.

Let's do one last example, problem, which is the average momentum:

\langle \hat{p}\rangle =\int^{upper}_{lower}{}{\psi }^*_{n^'}{\hat{x}\psi }_n\cdot \partial \tau =\int^L_0{}{\left(\left(n\pi \frac{x}{L}\right)right)}^*\cdot \frac\hslash{i}\frac{\partial }{\partial x}\left(n\pi \frac{x}{L}\ri

Several steps of simplification yield:

\[\langle \hat{p}\rangle =\int^{upper}_{lower}{}{\psi }^*_{n^'}{\hat{x}\psi }_n\cdot \partial \tau =\frac{2}{L}\frac\hslash{i}\frac{n\pi }{L}\int^L_0{}\left(n\pi \frac{x}{L}\right)cdot

▯ UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(n\pi \frac{x}{L}\right)cdot \partial x \nonumber \]

Since \(\int{}

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(ax\right)cdot cos(ax)\partial x=-\frac{1}{4a}cos\left(2ax\right)\) we find that:

\[\langle \hat{p}\rangle ={\frac{2\hslash n\pi }{iL^2}\left\{-\frac{L}{4n\pi }cos\left(2n\pi \frac{x}{L}\right)\right\}]}^{x=L}_{x=0}=-\frac\hslash{2iL}

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(2n\pi \right)\ +\frac\hslash{2iL} \nonumber \]

And since \(

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(2n\pi \right)\ =0\) for n as a whole number we find that $\langle\hat{p}\rangle = 0$. Does this make sense? Very much so, because if the particle had some net momentum then it could escape the box. But, it can't, so every time it starts to move left it must hit the wall and move right. The net of the left- and right- motion cancel out completely, so the particle is stuck.

Conclusion. This is your first introduction to basic quantum theory. The most important things to learn are that models that describe particles use the same equations that describe vibrating strings, which is why quantum is often called wave mechanics. Operators are the questions and eigenvalues are the answers, whereby the answers come from the wavefunction models. In the next chapter you will learn a few more complex models and review the uncertainty principle, which is the most important implication of quantum mechanics. Good luck with that.

CHAPTER OVERVIEW

13: Potential Surfaces and the Heisenberg Uncertainly Principle

Inarguably the most recognized statement in quantum mechanics is, “You can’t know where something is and how fast it is going”, which is the Heisenberg uncertainty principle. However, the real meaning is more far-reaching and unfortunately complex than this statement reveals. The uncertainty principle exists due to the statistical nature of quantum mechanics, and the fact that different physical properties are connected to each other by the quantum mechanical operators that describe them. Furthermore, the Heisenberg uncertainty principle is dynamic. For example, let’s say that you know a quantum particle is trapped in a very small spot. As a result, you can’t know the velocity at all, which makes the speed (and kinetic energy) very high. Last, there are actually several different uncertainty principles beyond the famous one between position and speed.

Before we go further, we must first introduce more complex systems to study, which is dependent on the nature of the potential energy surface. In the process, we will understand why some dyes are red or green, discuss new materials such as “quantum dots”, and reveal new phenomenon such as tunneling.

13.1: Potential Energy Surfaces

13.1.1 The step

In the previous chapter we discussed the simplest potential surface possible, a one-dimensional flat surface that never ends. This was called the “freewave” example. Unfortunately, the Universe is usually quite a bit more complicated because potential energy exists and may look like a bumpy barrier or curvy parabola. Introduced here is literally the first step towards understanding more complex problems: the step potential shown in Figure 13.1. To the left is a flat potential energy surface; however, at x=0 a “bump” in the form of a finite barrier appears that continues to the right forever. The potential surface requires that the Schrödinger equation be solved in two parts, one for the particle left of the barrier or to the right:

$$x < 0\ (left) : \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_I\left(x\right) = E \cdot \psi_I\left(x\right)$$

$$x > 0\ (right) : frac{-}\hbar^2 2m \frac{\partial^2}{\partial x^2}\psi_{II}\left(x\right) + V_0 \cdot \psi_{II}\left(x\right) = E \cdot \psi_{II}\left(x\right)$$

As a result we have to solve the Schrödinger equation twice. However, it is important to note that there is just one wavefunction that has a single energy. Furthermore, the wavefunction must be smooth and continuous.

The potential energy surface is flat to the left of the barrier, and we already know that the proper wavefunction for a flat potential is the “freewave”:

$$\psi_I = A \cdot e^{ik_1x} + B{\cdot}e^{-ik_1x}$$

The wavevector k_1 can be found by rearranging the Schrödinger equation: $\frac{\partial^2}{\partial x^2}\psi_I\left(x\right) = \frac{2mE}{\hbar^2} \cdot \psi_I\left(x\right)$, which makes $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$. Now as for the 2^{nd} region, we first rearrange the Hamiltonian as:

$$x > 0\ (right) : frac{-}\hbar^2 2m \frac{\partial^2}{\partial x^2}\psi_{II}\left(x\right) = \left(E - V_0\right) \cdot \psi_{II}\left(x\right)$$

Here we see that the Schrödinger equation to the right of the barrier is no different that to the left, albeit with a reduced energy due to the potential. Furthermore, the potential surface to the right is flat, so the same “freewave” solution applies albeit with a different momentum wavevector k_2:

$$\psi_{II} = C \cdot e^{ik_2x} + D{\cdot}e^{-ik_2x}$$

The wavevector k_2 can be found by simply replacing ” E ” in k_1 with $\left(E - V_0\right) : k_2 = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$. It is apparent that $\mathrm{k}_2 < \mathrm{k}_1$, and as a result if the particle has enough energy to cross the barrier the transmitted wavefunction’s de Broglie wavelength must increase. This makes sense since the k’s are related to the kinetic energy, which is the difference in the total energy minus the potential energy. Hence, when the particle crosses the barrier into region II it must be moving slower, which is evident from the longer wavelength.

13.1.1.1 Reflection and transmission

The next step is to question what can be learned from the finite step problem? The utility of this example is that it shows what happens when a quantum mechanical particle encounters a barrier. Up until now, you have been told that if a moving mass has enough kinetic energy it will traverses over a potential hill. Here, we will show you that light quantum mechanical particle such as an electron isn’t as cooperative.

First, we create a model whereby a 1-dimensional universe is created with a particle to the right of the barrier. The particle is thrown at the barrier, giving it a positive amount of momentum and energy. A wavefunction that describes a right-moving particle is:

$$\psi_I\left(x\right) = A \cdot e^{ik_1x}$$

When the particle strikes the barrier at x=0 it may reflect off of it, resulting in leftwards movement with the same kinetic energy and momentum due to conservation laws. Thus, the wavefunction in region I is:

$$\psi_I\left(x\right)=A\cdot e^{ik_1x}+B\cdot e^{-ik_1x}$$

If the particle transmits over the barrier it can only continue on to the right:

$$\psi_{II}\left(x\right)=C\cdot e^{ik_2x}$$

If you wonder why there is no leftward moving e^{-ik_2x} “D-wave” in region 2, it’s because there are no other barriers in that region to reflect off of. As a result, if the particle crosses into region II it will forever more move to the right. We refer to the expression $A\cdot e^{ik_1x}$ as the incoming “A-wave”, $B\cdot e^{-ik_1x}$ as the reflected “B-wave” and $C\cdot e^{ik_2x}$ as the transmitted “C-wave”. This is because the probability amplitude of the incoming wave is:

$$\left|A\cdot e^{ik_1x}\right|^2=\left|A\right|^2\cdot e^{-ik_1x}\cdot e^{ik_1x}=\left|A\right|^2\cdot e^0=\left|A\right|^2$$

The probability of reflecting is related to $\left|B\right|^2$ and likewise the probability of transmission is related to $\left|C\right|^2$.

The finite step potential can be used to calculate whether a quantum object transmits through or reflects off of a barrier. The reflection is the probability that a wave turns left divided by the probability it was moving right to begin with. Due to the fact that the absolute value of a wavefunction is related to probability we can define the reflection (R) as: $R=\frac{\left|B\right|^2}{\left|A\right|^2}$ and thus we must find expressions for the coefficient A and B as a function of energy. First, we invoke a stipulation that wavefunctions must be smooth and continuous at x=0, which is the boundary of the step potential. This gives us two equations to solve for our two unknowns:

$\psi_{I,(x=0)}=\psi_{II,(x=0)}$ (continuous) and: $\frac{\partial\psi_{I,(x=0)}}{\partial x}=\frac{\partial\psi_{II,(x=0)}}{\partial x}$ (smooth)

While these relationships are enough for us to solve the problem, there is a shortcut that is very helpful. What you do is to divide the smooth equation: `{{\psi }_I}^'={{\psi }_{II}}^'` by the continuous one: $\psi_I=\psi_{II}$ at the boundary:

`\[\frac`

ParseError: "}" expected (click for details)

ParseError: "}" expected (click for details)

`\nonumber \]`

(For those readers who are mathematically inclined, this is the log derivative `\partial \ln \left(\psi \right)=\frac{{\psi }^'}{\psi }`)

When we insert the equations and make x=0 we are left with:

$$\frac{A\cdot ik_1e^0-B\cdot ik_1e^0}{A\cdot e^0+B\cdot e^0}=\frac{C\cdot ik_2e^0}{C\cdot e^0}$$

Since $e^0=1$ and the C’s on the right cancel:

$$k_1A-k_1B=k_2A+k_2B$$

which can be rearranged to reveal:

$$\frac{B}{A}=\frac{k_1-k_2}{k_1+k_2}=\frac{\sqrt{E}-\sqrt{E-V_0}}{\sqrt{E}+\sqrt{E-V_0}}$$

To study this result we must create a model with realistic parameters. As such, we describe an electron (m=9.109×10^{-31} kg) striking against a $V_0=1$ electron volt step (an electron volt is the energy an electron experiences travelling through a 1 Volt potential, $1\ eV=1.602\times10^{-19}\ J$). Plotted in Figure 13.2 is the reflection and transmission as a function of the energy of the particle, where the transmission is simply 1-R. If the particle’s energy is less than the 1 eV barrier then it will always reflect. This makes sense, and mathematically results from the fact that $\sqrt{E-V_0}$ is an imaginary number which makes R $=\frac{(k_1-k_2)\cdot(k_1-k_2)^*}{(k_1+k_2)\cdot(k_1+k_2)^*}=\frac{E+E-V_0}{E+E-V_0}=1$. However, if the particle has enough energy to get over a barrier, *it may or may not*! The only thing that the particle can do to improve the odds of transmission is to strike the barrier with as much energy as possible.

13.1.1.2 Wavefunctions

The fact that $k_2 \sim \sqrt{E-V_0}$ is an imaginary number if $E<V_0$ has implications for the wavefunction in region II. If we substitute k_2=i\cdot k^'_2, where k^'_2 is a real positive number into the wavefunction we find:

{\psi }_{II}\left(x\right)=C\cdot e^{i^2\cdot k^'_2x}=C\cdot e^{-k^'_2x} \nonumber

Here we see that the wavefunction is exponentially decaying into the barrier. This is why the reflection has to be 100%, because the particle can't keep moving to the right into region II. It is interesting to note that the particle has some probability to travel though the barrier even though it doesn't have the energy to move into region II at all. We next ask, what if the barrier was thin such that the particle's wavefunction didn't completely decay before exiting the other side?

13.1.2 The finite barrier and tunneling

The next step up in complexity is the step potential that steps back down after a length of L. As shown in Figure 13.3, we might find that a particle wavefunction with an energy less than the potential might not decay to 0 before it reaches the end of the barrier. This means that the particle has some probability to travel through, despite not having enough energy to do so, and continues on to the right forevermore. This is called tunneling, and you may have heard that this phenomenon means you can walk through a door. This is in fact true; however, the probability that you can do so is exceptionally low.

As in the previous example there are three regions; to the left are the on-coming A-wave and the reflected B-wave. In region III we find the transmitted E-wave, $\psi_{III}\left(x\right)=E\cdot e^{ik_1x}$, which represents the particle that has tunneled through the barrier. In between are the "C" and "D" waves, where the C-wave represents the particle penetrating the front of the barrier while the D-wave is a reflection off the back end. You might wonder why there is a D-wave, after all, the particle isn't encountering a higher potential barrier. The reason that the D-wave exists is because all interfaces cause reflection, even when one traverses from a higher potential to a lower one. For example, you can see your reflection in a car with new black paint, right? This is the same phenomenon.

The transmission probability is $T=\frac{|E|^2}{|A|^2}$, and to calculate it we must determine all the wavefunctions' coefficients as a function of energy. This can be done using the boundary conditions for smooth and continuous wavefunctions at positions x=0 and x=L. Unfortunately, this is a very time-consuming calculation due to the overuse of algebraic manipulation, and we won't go through that here. Rather, we simply present the end result in Figure 13.4. Unlike the step potential, there is a small chance for transmission to occur for energies less than the barrier due to tunneling as discussed previously; this is highlighted in green in Figure 13.4. At the same time, transmission is not assured if there is enough energy to go over the barrier is in the step potential. Most interesting of all is the wavy structure in the transmission as a function of increasing energy see in Figure 13.4. Occasionally the transmission reaches 100%; these are called "resonances" and they occur when the particle's de-Broglie wavelength is the same as the length of the barrier. Such behavior is frequently observed in sophisticated spectroscopy experiments, especially in X-ray studies of gas atoms and molecules.

13.1.3 The particle in a box

The next model problem on our list is the "particle-in-a-box", which has a potential energy surface defined in three regions by:

$$x<0 V\left(x\right)=\infty$$

$$0\le x\le L\ V\left(x\right)=0$$

$$x>L V\left(x\right)=\infty$$

This surface is shown in Figure 13.5. We seek a solution to the Schrödinger equation in the form of a wavefunction, which must be 0 everywhere outside the box because the particle couldn't be found there unless it has an infinite amount of kinetic energy. Thus, we don't need to concern solving the wavefunctions anywhere except region II, the interior of the box. Since region II has a flat potential surface, the wavefunction must be the same as the freewave solution:

$$\psi_{II}\left(x\right)=A\cdot e^{ik\cdot x}+B\cdot e^{-ik\cdot x}$$

The coefficients A and B must be determined, as well as the wave vector k. Defining a wavefunction in such a manner is generally resolved by satisfying boundary conditions; additionally the wavefunction must be normalized. For example, the fact that a wavefunction must be continuous requires that $\psi=0$ at the left (x=0) and right sides (x=L) of the box. The fact that the wavefunction must disappear at x=0 requires:

$$A \cdot e^{0} + B \cdot e^{0} = 0$$

and as a result $B = -A$. This implies that the wavefunction is a sine wave as $sin\left(k \cdot x\right) = A \cdot e^{ik \cdot x} - A \cdot e^{-ik \cdot x}$ if $A = \frac{1}{2i}$. Thus, the boundary condition reveals that:

$$\psi_{II}\left(x\right) = sin\left(k \cdot x\right)$$

Now we have to apply the second boundary condition at x=L:

$$sin\left(k \cdot L\right) = 0$$

This can only be true if $k_1 L = n\pi$, allowing us to solve for the wave vector:

$$k = \frac{n\pi}{L}$$

where n is an integer that goes from 1,2,3… As a result, the wavefunction is:

$$\psi_{II}\left(x\right) = N \cdot sin\left(\frac{n\pi}{L}x\right)$$

and 0 everywhere else due to the infinite potential.

13.1.3.1. Orthonormalization

The last piece of the puzzle is to solve for N, the normalization constant. To go about this, we write the condition for normalization $\int |\psi|^{2} = 1$ and insert the result thus far:

$$N^{2}\int_{0}^{L} sin^{2}\left(\frac{n\pi}{L}x\right)\partial x = 1$$

which allows N to be defined as:

$$N = \frac{1}{\sqrt{\int_{0}^{L} sin^{2}\left(\frac{n\pi}{L}x\right)\partial x}}$$

We solved the integral by looking it up on the internet: $\int_{0}^{L} sin^{2}\left(\frac{n\pi}{L}x\right)\partial x = \frac{L^{2}}{4}$, which means $N = \sqrt{\frac{2}{L}}$ and the full particle in a box wavefunction is: $\psi_{II}\left(x\right) = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi}{L}x\right)$. These wavefunctions are also orthogonal to each other: `\int{}{\psi }^*_{{\upsilon }^'}{\psi }_{\upsilon }\partial x={\delta }_{{\upsilon }^',\upsilon }`, where `{\delta }_{{\upsilon }^',\upsilon }` is the Kronecker delta function that is `{\delta }_{{\upsilon }^',\upsilon }=1` if `{\upsilon }^'=\upsilon`, which is the normalization condition, and `{\delta }_{{\upsilon }^',\upsilon }=0` if `{\upsilon }^'\neq \upsilon`. This is a result of the fact that the Hamiltonian is a Hermitian operator (see Ch. 12, section 12.4.5).

13.1.3.2 Energy levels

In our previous examples, we were able to solve the wavefunction for any value of energy. As a result, these models are called “unbounded”. The particle in a box energy is different, we can see after it is calculated from the Hamiltonian acting on the wavefunction via $\hat{H}\psi = E\psi$:

\[\frac{-\hslash^2}{2m}\frac

ParseError: invalid DekiScript (click for details)

sin\left(\frac{n\pi }{L}x\right)=\frac{\hslash^2n^2{\pi }^2}{2mL^2}\sqrt{\frac{2}{L}}sin\left(\frac{n\pi }{L}x\right)=E\cdot {\psi }_{II}\left(x\right) \nonumber \]

and thus:

$$E = \frac{n^{2}\hbar^{2}\pi^{2}}{2mL^{2}} = \frac{n^{2}h^{2}}{8mL^{2}}$$

where we used the fact that $\hbar^2 = \frac{h^2}{4\pi^2}$. Given that n is an integer, we see that the particle in a box cannot have just any energy. There are gaps between the ground state (n=1) and the 1^{st} excited state (n=2), which is why we refer to the system as “bounded”. The energy comes in discrete steps, or quanta, which is where quantum mechanics gets its name! Anther facet of quantum mechanics is the need for an integer quantum number, here n, which can delineate the ground state from all the excited states. Quantum numbers will appear in all the systems we will study from now on and are usually part of the equation for energy. It is interesting to note that the ground state has some finite kinetic energy, called the “zero point energy”. As we will discuss later in this chapter zero point energy is due to the Heisenberg uncertainty principle.

The particle in a box describes several phenomena, many of which can be seen with your own eyes! Shown in Figure 13.5B are the spectra of several cyanine dyes, which reveal lower energy absorptions as the dye becomes longer. An analogy can be made that the number of alternating double bonds in the center of the cyanine molecule is the same as the length L of the particle in a box. It should be noted that the absorptions are not related to the energy of a single quantum level, rather, the differences between the ground and 1^{st} excited state levels. For a particle in a box that quantity is: $\Delta E = \frac{(n=2)^2 h^2}{8mL^2} - \frac{(n=1)^2 h^2}{8mL^2} = \frac{3h^2}{8mL^2}$, which reveals an expected 1/L^2 dependence to the absorption between states as the box size changes.

Shown in Figure 13.6 is a more dramatic example using nanotechnology, specifically semiconductor CdSe quantum dots. The emission of the particles can be tuned to lower (redder) energies by increasing the diameter of the particle on the order of just a few nanometers. And as solid-state materials, quantum dots are significantly more robust against degradation from the environment, which is why they are being incorporated into displays including television sets!

13.1.3.3 The particle in the finite box

Imagine the particle in a box potential surface where the barriers to the outside are not infinite as shown in Figure 13.7A. Note that we have centered the box at x=0 for mathematical convenience as you will see. There are two issues to consider, namely that there are three regions each of which has a different wavefunction. As in the previous example, we will use boundary conditions to solve for the wavefunctions and allowed energy levels. Furthermore, it should be noted that there are bound solutions for $E<V_0$, meaning that the energy is quantized into discrete values. For energies greater than the potential trap ($E>V_0$) the solutions are unbound, meaning that the wavefunctions are just waves and any energy is allowed. We won’t consider that situation and will instead only study the case where $E<V_0$.

Let’s first attempt to solve the ground state wavefunction. The potential has even symmetry about x=0, and as such we assume that the trap region also has even symmetry like a cosine function. As a result, $\psi_{II}(x) = B \cdot cos\left(k_2 x\right)$, where the wavevector $k_2 = \sqrt{\frac{2mE}{\hbar^2}}$. If the particle penetrates into the barrier region I on the left it will continue in that direction, implying $\psi_I = A \cdot e^{k_1 \cdot x}$ where $k_1 = \sqrt{\frac{2m(V-E)}{\hbar^2}}$. Using the same logic $\psi_{III} = C \cdot e^{-k_1 \cdot x}$. As per the boundary conditions, the wavefunctions must be continuous and smooth at the region I/II boundary:

\(A\cdot e^

ParseError: EOF expected (click for details)

=B\cdot cos\left(-k_2\frac{L}{2}\right)\) and \(k_1\cdot A\cdot e^

ParseError: EOF expected (click for details)

={-k}_2\cdot B\cdot sin\left({-k}_2\frac{L}{2}\right)\)

and likewise for region II/III:

$B \cdot cos\left(k_2 \frac{L}{2}\right) = C \cdot e^{-k_1 \cdot \frac{L}{2}}$ and $-k_2 \cdot B \cdot sin\left(k_2 \frac{L}{2}\right) = -k_1 \cdot C \cdot e^{-k_1 \cdot \frac{L}{2}}$

Solving using log boundary conditions yields what is called a “transcendental” equation for k_1 and k_2:

$$tan\left(k_2 \frac{L}{2}\right) = \frac{k_1}{k_2}$$

The relationship above requires you to define the model system (length of the box, potential height, and mass of the particle) and then search for energies that equate the two sides using a computer. Once you know the allowed energies you can determine the A, B etc. coefficients and then plot the wavefunctions as shown in Figure 13.7A.

This model system can be applied to understand many real phenomena and can also be used to describe electrons in atoms. For the latter case, this works because an electron sees a hydrogen's proton like a trap- Coulomb's law keeps it close by since there is a huge energy penalty to be far away. The finite box can give us an idea about how chemical bonds work if we allow two boxes to get close to each other. Shown in Figure 13.7B are the ground and 1^{st} excited states for a particle between two finite boxes. It can be seen that the wavefunction "bunches" between the two traps in the ground state while a node prevents the same in the excited state. This represents ground state bonding and excited state antibonding orbitals!

13.2: Complex Potential Energy Surfaces- Vibration

We now take our first step into non-flat potential surfaces by studying the quantum mechanics of springs; this is called the harmonic oscillator problem. Incidentally, chemical bonds work just like springs. Two atoms form a bond along the “x” direction, with an equilibrium bond distance of x_0. Any displacement from equilibrium results in a linear restoring force: $F=-\frac{\partial V}{\partial x}=-k_f\left(x-x_0\right)$, the strength of which is dictated by the spring constant k_f. Since we want to know the potential energy V as a function of the position we note that $\frac{\partial V}{\partial x}--F(x)$ and integrate as follows:

$$\int \partial V=V(x)=-\int -k_f\left(x-x_0\right)\partial x=\frac{1}{2}k_f\left(x-x_0\right)^2$$

To place this in a quantum mechanical context we simply insert the position operator $\hat{x}$ as so: $\hat{V}=\frac{1}{2}k_f\left(\hat{x}-x_0\right)^2$, which likewise makes the potential energy an operator. And while we are ready to put this into the Schrödinger equation, however, before we do so there is a very small change that significantly simplifies everything. This is to simply drop the equilibrium distance x_0 from the potential energy operator as shown here:

$$\hat{V}=\frac{1}{2}k_f\left(\hat{x}-x_0\right)^2\rightarrow\frac{1}{2}k_f\hat{x}^2$$

The implication is that the position operator $\hat{x}$ is now interpreted as the bond’s displacement *away* from equilibrium. Thus, a positive $\langle\hat{x}\rangle$ means that the bond is stretched and a negative $\langle\hat{x}\rangle$ means compressed. There is one more issue to examine, which is the fact that the kinetic energy operator $\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ has the familiar factor of mass. However, when describing vibrational motion between two bonded atoms then it is no longer clear which atom’s mass should be used. The solution is to use the reduced mass: $\mu=\frac{m_1\cdot m_2}{m_1+m_2}$, where m_1 and m_2 are the masses of atoms 1 and 2, respectively.

13.2.1.1 Wavefunctions

With knowledge of the Schrödinger equation:

v	H_v	There is an interesting mathematical relationship that can be demonstrated with Hermite polynomials: $H_{v+1}=\frac{2x}{\alpha}\cdot H_v-2v\cdot H_{v-1}$ This is called a recursion and allows all the Hermite polynomials to be determined with just the first one: $H_{v=0}=1$.
0	1	
1	$\frac{2x}{\alpha}$	
2	$\frac{4x^2}{\alpha^2}-2$	
3	$\frac{8x^3}{\alpha^3}-\frac{12x}{\alpha}$	

Table 13.1 Hermite polynomials.

\[\frac{-\hslash^2}{2\mu }\frac

ParseError: invalid DekiScript (click for details)

^2\cdot \psi \left(x\right)=E\cdot \psi \left(x\right) \nonumber \]

we are ready to solve for the wavefunction ψ. This effort is somewhat complex; as such, we will simply assure you that the mathematics are tractable and that the wavefunctions are as shown in Figure 13.8. These solutions can be succinctly described using the following formula:

$$\psi_v(x) = N_v H_v e^{-\frac{x^2}{2\alpha^2}}$$

where $\alpha = \left(\frac{\hbar^2}{\mu k_f}\right)^{\frac{1}{4}}$, $v \to 0, 1, 2\ldots$ is the principal quantum number, $N_v = \left(\frac{1}{v!2^v\alpha\sqrt{\pi}}\right)^{\frac{1}{2}}$ is the normalization constant, and H_v are the Hermite polynomials listed in Table 13.1.

Let's turn our attention to the ground state wavefunction which has a bell-shape as shown in Figure 13.8. Subsequent excited states have additional nodes due to the Hermite polynomials; these increase the curvature and thus the kinetic energy of each state. Note how, in calculus, the double derivative found in the kinetic energy operator is called the "curvature" of a function! The Hermite polynomials also assures that the wavefunctions are orthogonal to each other.

There are many other quantum mechanical properties to examine, including the fact that $\langle\hat{x}\rangle = \int \psi_v^* \cdot x \cdot \psi_v \partial x = 0$ regardless of the state. From this we learn that the bond is on average at the equilibrium bond length, even in highly excited states. Calculation of the energy E as a function of principle quantum number v reveals the relationship: $E(v) = \left(v + \frac{1}{2}\right)\hbar\omega$, where ω is the angular frequency: $\omega = \left(\frac{k_f}{mass}\right)^{\frac{1}{2}}$. An important implication is the fact that the ground state has energy is finite: $E_{v=0} = \frac{1}{2}\hbar\omega$. Like the particle in a box this is the zero-point energy, and it means that the atoms are always vibrating. There are other interesting analogies to the particle in a box problem; the wavefunctions look surprisingly similar including the way they pick up additional nodes in each excited state. One significant difference is that the harmonic oscillator energies are linear with the principal quantum number, $E \propto v$, whereas the particle in a box is quadratic in proportion to its principal quantum number, $E \propto n^2$.

13.2.1.2 Kinetic Isotope Effect and Turning Points. An interesting implication of the zero-point energy is that it is inversely proportional to the reduced mass. This has an effect on the rate of a chemical reaction as dictated by the ΔG^* barrier. Take for example the breaking of a carbon-hydrogen (R_3C-H) bond. Given that the reduced mass is less for a C-H bond vs. the deuterated analog C-D, there is a smaller barrier for the C-H bond to break as shown in Figure 13.9 A. As a reaction rate is proportional to the barrier $k \sim e^{-\Delta G^*}$ (like the Arrhenius equation), the relative rates of reaction involving a proton are generally faster to the same with deuterium according to the formula:

$$\frac{k_{CH}}{k_{CD}} \sim \frac{e^{-\Delta G^*_{CH}}}{e^{-\Delta G^*_{CD}}}$$

While this ratio can be as high as 8×, in reality there are many other factors in play and as such the kinetic enhancement can be less. Regardless, the kinetic isotope effect is quite useful because it gives organic chemists a method to investigate which bonds break in a reaction. Thus, it is often used for mechanistic analysis.

The wavefunction shown in Figure 13.8 are for a carbon monoxide molecule, which has a high spring constant k_f=1860 N/m. As such, the bond doesn't stretch far as evident from the fact that the wavefunctions do not have significant amplitude past ~1/2 Bohr, where a Bohr is a unit of length and is equal to 0.53 Å. In contrast, I_2 has a very weak bond as evident from a k_f=170 N/m, and as such it can stretch almost twice as much as CO. Regardless of how strong a bond is, the atoms have a way of stretching further than they should as revealed by the vibrational potential energy surface and ground state wavefunction shown in Figure 13.9 B. The point where the total energy is equal to the potential, where there must be no more kinetic energy:

$$\frac{1}{2}\hbar\omega = \frac{1}{2}k_f \cdot x_{tp}^2 \to x_{tp} = \pm\sqrt{\frac{\hbar\omega}{k_f}}$$

This is marked in the figure as the turning point (x_{tp}), which is where a normal spring would stretch to the point where it stops and starts to compress back. However, this isn't true for the quantum mechanical spring, as the wavefunction has some finite value for any x. As a result:

$$\int_{x_{tp}}^{\infty} |\psi_{v=0}|^2 \partial x = 0.078$$

Consequently, there is ~8% chance that a bond will stretch past the point of having no kinetic energy, which is analogous to tunneling discussed previously. Does this mean that the kinetic energy is in fact negative? What does negative kinetic energy motion look like? This is one of the wonders of quantum mechanics as there is no analogy to our everyday experiences that would help describe this.

13.3: Uncertainty and Superposition- Wavefunctions as Waves

The uncertainty principle, “you can’t know where something is and how fast it is going,” is one of the most important aspects of quantum mechanics. In our explanation of this phenomenon, we will study bell-shaped wavefunctions that are centered inside a box that goes from $0 \leq x \leq L$:

\[\frac{1}

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\ \nonumber \]

We will analyze two different wavefunctions, a narrow one that we call “localized” and a wide one that we call “delocalized”. Hopefully it is intuitively clear that there is more certainty in the position of the localized wavefunction compared to the delocalized state.

In the previous chapter we introduced the idea that an eigenfunction ψ of one operator can be expressed as a linear combination of the eigenfunctions $\mathit{\Phi}_n$ of a different operator. This is called a superposition:

$$\psi = \sum_n c_n \cdot \mathit{\Phi}_n$$

and for our purposes we will make all the $\mathit{\Phi}_n$’s freewave states:

$$\mathit{\Phi}_n = e^{ik_nx}$$

were the wavevector k is defined so that the freewaves fit in the box: $k_n = \frac{n\pi}{L}$ and n = ±1, ±2, ±3, etc. The bell-shaped wavefunctions and the freewaves are all graphed in Figure 13.10.

An example of a superposition is shown in Figure 13.11, where we see that the wider delocalized bell-shaped state can be equated to a sum of wave states weighted by an appropriate constant. Here only three waves are needed to create a superposition that appears identical to the delocalized function as shown in Figure 13.11. A very different result is observed with the localized state shown in Figure 13.12. Here, it is necessary to sum at least 5 wave states to provide a reasonable representation of the localized function. Even then the overlap isn’t as good as observed with the delocalized state in Figure 13.11 despite the fact that more functions were used!

Now you are probably asking- what any of this has to do with the uncertainty principle? To answer, let’s now measure the momentum of the localized and delocalized states. The measurements require us to do an experiment, and we will be repeat the experiment several times to statistically quantify the average value and standard deviation which is the uncertainty. This is necessary because it is reasonable to expect some variation in the measurements from experiment to experiment. In fact, we contend that each measurement will return the momentum of one of the wave states, which is $\hbar k_n = \hbar \cdot \frac{n\pi}{L}$, with a probability $c_n{}^2$. Thus, measuring the momentum from the delocalized state will return one of the three composing wave state’s momenta with corresponding probabilities of $c_1{}^2$, $c_2{}^2$, or $c_3{}^2$. We can also calculate the expectation value of the momentum via:

$$\langle p\rangle = |c_1|^2 \cdot \hbar k_1 + |c_2|^2 \cdot \hbar k_3 + |c_3|^2 \cdot \hbar k_5$$

In contrast, when the same experiment is repeated on the localized state, each measurement returns one of five values of wave momenta with corresponding probabilities of $c_1{}^2$, $c_2{}^2$, $c_3{}^2$, $c_4{}^2$, or $c_5{}^2$.

Do you have more or less confidence in the measurement of the momentum of the delocalized vs. localized state? Of course, there is greater certainty for the delocalized state since each measurement returns one of just three values, and probably we won’t have to make too many measurements before we are comfortable with the average. However, measuring the localized state is problematic since the result varies more from experiment to experiment! This is due to the fact that the experiment samples from five different wave states, and thus we will have to make more measurements to have the confidence in the result. We conclude that the certainty in position is anticorrelated to the certainty in momentum. This is in fact the Heisenberg uncertainty principle, “you can’t know where something is and how fast it’s going at the same time.” Mathematically, this is expressed by the variance in the function, the square root of which is the standard deviation (\sigmaup) you may recall from your introduction into statistics; more on this later.

The above demonstration involved some approximations and was meant to give you a graphical description of uncertainty in quantum mechanics. Now, we must slog through more rigorous mathematics. First, let’s define uncertainty via the variance, and we will start with the variance in position:

$$\langle Var\left(\hat{x}\right)\rangle = \langle \frac{1}{N-1}\sum_{i=1}^{N}{\left(x-\underline{x}\right)}^2\rangle = \langle \hat{x}^2\rangle - {\langle \hat{x}\rangle}^2$$

You may be familiar with this formula from your first introduction to statistics, and also note that the expressions $\langle \hat{x}\rangle$ and $\langle \hat{x}^2\rangle$ are expectation (average) values.

Let’s calculate the variance in the position for our bell-shaped wavefunction: $\frac{1}{\sqrt{2\pi\sigma}}\,e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{2\sigma^2}}$ using the $\hat{x}$ and $\hat{x}^2$ operators.

\[\langle \hat{x}\rangle =\int^{\infty }_{-\infty }{}{\psi }^*\cdot \hat{x}\cdot \psi \cdot \partial x=\int^{\infty }_{-\infty }{}{\left(\frac{1}

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\right)}^*\cdot x\cdot \frac{1}

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \partial x \nonumber \]

$$=\frac{1}{\sqrt{2\pi\sigma^2}}\int_{-\infty}^{\infty} x\cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}\cdot\partial x=\frac{L}{2}$$

Next: $\left\langle \hat{x}^2\right\rangle=\frac{1}{\sqrt{2\pi\sigma^2}}\int_{-\infty}^{\infty} x^2\cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}\cdot\partial x=\sigma^2+\left(\frac{L}{2}\right)^2$

As a result: $\left\langle \hat{x}^2\right\rangle-\left\langle \hat{x}\right\rangle^2=\sigma^2+\left(\frac{L}{2}\right)^2-\left(\frac{L}{2}\right)^2=\sigma^2$. This is a perfectly sensible result, and in fact it is a standard statistical definition that the variance of a bell-shaped curve is σ^2!

Let's determine the variance in momentum, $var\left(\hat{p}\right)=\left\langle p^2\right\rangle-\left\langle p\right\rangle^2$:

\[\langle \hat{p}\rangle =\int^{\infty }_{-\infty }{}{\psi }^*\cdot \hat{p}\cdot \psi \cdot \partial x=\int^{\infty }_{-\infty }{}{\left(\frac{1}

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\right)}^*\cdot \frac\hslash{i}\frac{\partial }{\partial x}\frac{1}

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \partial x= \nonumber \]

$$\frac{\hbar}{i\sqrt{2\pi\sigma^2}}\int_{-\infty}^{\infty} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}}\cdot\frac{\partial}{\partial x}e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}}\cdot\partial x=\frac{\hbar}{i\sqrt{8\pi}\sigma^3}\int_{-\infty}^{\infty}\left(x-\frac{L}{2}\right)\cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}\cdot\partial x=0$$

No average momentum, which shouldn't be interpreted as the particle not moving. Rather, the particle can move left or right equally averages out to 0. Next, calculating the average of the momentum squared takes a bit more effort:

\[\langle {\hat{p}}^2\rangle =\int^{\infty }_{-\infty }{}{\psi }^*\cdot {\hat{p}}^2\cdot \psi \cdot \partial x=-\hslash^2\int^{\infty }_{-\infty }{}{\left(\frac{1}

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\right)}^*\cdot \frac

ParseError: invalid DekiScript (click for details)

e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \partial x= \nonumber \]

\[\frac{-\hslash^2}{\sqrt{2\pi {\sigma }^2}}\int^{\infty }_{-\infty }{}e^{\frac{-{\left(x-\frac{L}{2}\right)}^2}{4{\sigma }^2}}\cdot \frac

ParseError: invalid DekiScript (click for details)

\cdot \partial x=\frac

ParseError: invalid Primary (click for details)

\cdot \partial x=\frac{\hslash^2}{4{\sigma }^2} \nonumber \]

As a result, the variance in momentum is: $\left\langle \hat{p}^2\right\rangle-\left\langle \hat{p}\right\rangle^2=\frac{\hbar^2}{4\sigma^2}-0^2=\frac{\hbar^2}{4\sigma^2}$

The results reveal that the uncertainty in position and momentum are anticorrelated; the position uncertainty scales as σ^2, however, the momentum uncertainty is inversely proportional to σ^2. Thus, if the particle is localized in position then there is an increasing uncertainty in momentum. This becomes clearer when we multiply the two variances:

$$Var\left(\hat{x}\right)\cdot Var\left(\hat{p}\right)=\sigma^2\frac{\hbar^2}{4\sigma^2}=\frac{\hbar^2}{4}$$

which results in a constant. This is, in fact, the mathematical version of the Heisenberg uncertainty principle.

13.3.1 The Heisenberg Uncertainty Principle. There is a math theorem that can assist us with understanding the previous example called the Cauchy-Schwartz inequality. It is analogous to the fact that a dot product between two vectors: $\overrightarrow{a}\cdot\overrightarrow{b}=|a|\,|b|\,cos\left(\theta\right)$, is equal to or less that $|a|\,|b|$ due to the fact that the maximum $cos\left(\theta\right)$ can be is 1. This concept allows us to express the Heisenberg uncertainty principle as an equation:

$$Var\left(\hat{x}\right)\cdot Var\left(\hat{p}\right)\geq\frac{1}{4}\left|\left\langle\left[\hat{x},\hat{p}\right]\right\rangle\right|^2$$

where a new mathematical entity called the commutator appears on the right:

$$[\hat{x},\hat{p}]=\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}$$

The expectation value of the commutator is simply $\langle[\hat{x},\hat{p}]\rangle=\langle\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}\rangle=\langle\hat{x}\cdot\hat{p}\rangle-\langle\hat{p}\cdot\hat{x}\rangle$. Normally, expectation values have to be evaluated using specific wavefunctions. However, there is a simple and general way to evaluate $\langle[\hat{x},\hat{p}]\rangle$. This works by applying a “dummy” ψ on the right of the operators, allowing them to act on it and then dividing ψ out on the left:

$$\langle[\hat{x},\hat{p}]\rangle=\frac{1}{\psi}[\hat{x},\hat{p}]\,\psi$$

Inserting $[\hat{x},\hat{p}]=\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}$ and the definition of the momentum operator $\hat{p}=\frac{\hbar}{i}\frac{\partial}{\partial x}$ and $\hat{x}=x$ into the above yields:

$$\langle[\hat{x},\hat{p}]\rangle=\frac{1}{\psi}(\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x})\,\psi=\frac{\hbar}{i}\frac{1}{\psi}\left(x\cdot\frac{\partial}{\partial x}-\frac{\partial}{\partial x}\cdot x\right)\psi=\frac{\hbar}{i}\frac{1}{\psi}\left(x\cdot\frac{\partial}{\partial x}\psi-\frac{\partial}{\partial x}\cdot x\cdot\psi\right)$$

Noting the need for the product rule on the right-hand side results in:

`\langle \left[\hat{x},\hat{p}\right]\rangle =\frac\hslash{i}\frac{1}{\psi }\left(x\cdot {\psi }^\'-x\cdot {\psi }^\'+\psi \right)=\frac\hslash{i}\frac{\psi }{\psi }=\frac\hslash{i} \nonumber`

This can be re-inserted into the expression from our previous formula: $\frac{1}{4}|\langle[\hat{x},\hat{p}]\rangle|^2=\frac{1}{4}\left|\frac{\hbar}{i}\right|^2=\frac{\hbar^2}{4}$ to yield:

$$Var\,(\hat{x})\cdot Var\,(\hat{p})\geq\frac{\hbar^2}{4}$$

13.3.1.1 Interpretation. The Heisenberg uncertainty principle states that once cannot know position and momentum, or speed, of a quantum mechanical object simultaneously. Better knowledge of position increases the uncertainty in momentum, and the only way the uncertainty in momentum can rise is for the average momentum to increase. To understand why, take for example a car going 10 miles per hour on average. Do you have more, or less uncertainty in its speed compared to a car going 100 mph on average? Of course, there must be greater uncertainty in the velocity of the faster moving car because it has considerably more leeway for its momentum to vary more. As a result, a greater uncertainty in momentum must be associated with greater momentum in general, which also means that the object must have greater kinetic energy. Thus, if a delocalized quantum mechanical particle, such as an electron in an aromatic ring, becomes localized on a single atom, then it’s kinetic energy must increase. This is why quantum particles like to become delocalized if possible, and also describes why the energy of a particle in a box increases if the box is smaller: $E\propto\frac{1}{L^2}$. The Heisenberg uncertainty principle is often used to explain nanoscale phenomena including the size dependence of the emission of quantum dots shown in Figure 13.6.

The commutator $[\hat{x},\hat{p}]=\hat{x}\cdot\hat{p}-\hat{p}\cdot\hat{x}$ can be interpreted in a way that makes sense out of the uncertainty principle. Since $[\hat{x},\hat{p}]\neq 0$, then $\langle\hat{x}\cdot\hat{p}\rangle\neq\langle\hat{p}\cdot\hat{x}\rangle$, and as a result measuring the position of a particle, and then its momentum, would yield a different result than if you first measured momentum and then position! However, there is no “right” way to do this, so the result is arbitrary depending on what order the experimentalist happened to use when making measurements on small, quantum mechanical particles. Thus, there is uncertainty.

13.3.1.1 Generalization. The Heisenberg uncertainly principle simply states that, at best, the product of the position and momentum variances is no more than $\frac{\hbar^2}{4}$. If one has a specific system with a known wavefunction then one has to evaluate the product of $var\,(\hat{x})$ and $var\,(\hat{p})$ directly. In fact we did so in the previous section using the bell-shaped wavefunction and found that the equality held for the uncertainty principle: $var\,(\hat{x})\cdot var\,(\hat{p})=\frac{\hbar^2}{4}$. These Gaussian functions are considered special as a result and are often referred to as “minimum uncertainty” wavefunctions. In some of the problem set questions at the end of this chapter you will find that the products of the variances in position and momentum for various particle in a box wavefunctions are indeed greater than $\frac{\hbar^2}{4}$.

It is important to realize that, while the position / momentum uncertainty principle is “famous”, there are in fact a very large number of other examples. For any two operators $\widehat{\Omega}_1$ and $\widehat{\Omega}_2$ the uncertainty principle states:

$$Var\left(\widehat{\Omega}_1\right)\cdot Var\left(\widehat{\Omega}_2\right)\geq\frac{1}{4}\left|\langle\left[\widehat{\Omega}_1,\widehat{\Omega}_2\right]\rangle\right|^2$$

and as a result there is uncertainty if $\left[\widehat{\Omega}_1\,,\widehat{\Omega}_2\right]\neq 0$. We will find examples using quantum rotational motion and when describing the spin angular momentum of electrons. Here is one you can try on your own; determine the uncertainty between the position $\hat{x}=x$ and kinetic energy operators $\widehat{KE}=\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. If you evaluate the uncertainty principle by simplifying the commutator using: $\left[x,\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\psi$ one finds that: $Var\,(\hat{x})\cdot Var\left(\widehat{KE}\right)\geq\frac{\hbar^2}{4m}|\langle\hat{p}\rangle|^2$

This at first may appear hard to interpret as the commutator is an operator rather than a constant. What is meant here is that the uncertainty between position and kinetic energy is dependent on the expectation of momentum. Thus, if the particle has no momentum then there is a potential for there to be no uncertainty between position and kinetic energy. However, the uncertainty increases as the particle is moving faster and faster.

There is one last implication of the uncertainty principle, which is that the eigenfunctions of one operator $\widehat{\Omega}_1$ cannot be the same as the other operator $\widehat{\Omega}_2$ if $\left[\widehat{\Omega}_1\,,\widehat{\Omega}_2\right]\neq 0$. This is generally a topic that one encounters when studying more advanced quantum mechanical phenomena such as rotation, spin angular momentum and the spin-orbit effect discussed in latter chapters.

Conclusions. In this chapter we showed how increasing the complexity of model systems through their potential energy surfaces reveals new quantum phenomena. Specifically, how a particle may bounce off a wall even if it is higher than it. Also, quantum particles can tunnel through barriers like they have a negative kinetic energy. Furthermore, the kinetic energy of a particle increases if we trap it, which is why we can change the color of a quantum dot by changing its size. While this chapter discusses most of the basic principles of quantum mechanics, in the next few chapters we are going to move away from one dimensional example problems and discuss real systems leading up to the hydrogen atom. To do so we have to understand how quantum mechanics works in 3D and how to deal with rotational motion.

CHAPTER OVERVIEW

14: Multidimensional Quantum Mechanics and Rotation

We have focused on single dimensional systems thus far in our discussion of quantum mechanics. However, the Universe is three-dimensional, and as such we need to study 3D quantum mechanics. To begin this chapter we will show that the inclusion of extra dimensionality causes an unfortunate increase in complexity of the kinetic energy operator. And while this is not terribly difficult for a particle in a box problem (or we should rather say particle in a cube), it can become onerous once we start to work with spherical objects such as atoms. You will see when we start describing rotating quantum particles in the 2^{nd} half of this chapter. Regardless of the nature of our model problems, one of the most important results is the fact that multidimensionality introduces energetic degeneracy (two or more quantum states with the same energy). Degeneracies have significant impact on many areas of science as they have a substantial effect on the physical properties of chemicals and materials.

14.1: Multidimensional Free waves and the Particle in a Cube

We begin our understanding on multidimensional quantum mechanics with the kinetic energy operator $\frac{-\hbar^2}{2\cdot mass}\frac{\partial^2}{\partial x^2}$, as most of the complexity of quantum mechanics originates from here as we saw back in Ch. 12. The operator must be augmented with additional terms, likely the same expression except with y: $\frac{-\hbar^2}{2\cdot mass}\frac{\partial^2}{\partial y^2}$ and z: $\frac{-\hbar^2}{2\cdot mass}\frac{\partial^2}{\partial z^2}$. Now the question is how- are these terms added into the operator? Or do they all multiply? Let's use an analogy- recalling the equipartition theorem from your earlier introduction to thermodynamics, the energy of a particle increases by ½k$_B$T for every degree of freedom that particle has. The ability of a particle to move in x, y and z counted as three degrees of freedom, and as a result all the ½k$_B$T energies were summed. This leads us to conclude that the kinetic energy operator must likewise sum energies for each accessible dimension, which is:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

This expression is the full 3D kinetic energy operator, and we will use it to revisit our old problems of the freewave and particle in a box once we know a little bit more about how to solve the wavefunctions.

14.1.1. Multidimensional wavefunctions and separability in the 3D freewave problem

With the kinetic energy operator in hand, let's solve a simple system such as the freewave in 3D, which describes a particle that moves in any direction, forever, without encountering any potential energy. The Schrödinger equation for the 3D freewave is then:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\mathit{\Psi}(x,y,z)=E\cdot\mathit{\Psi}(x,y,z)$$

To make further progress we must know more about the total wavefunction $\mathit{\Psi}(x,y,z)$. Could it be a simple summation of "mini" wavefunctions in different dimensions: $\mathit{\Psi}(x,y,z)=\mathit{\Psi}_x(x)+\mathit{\Psi}_y(y)+\mathit{\Psi}_z(z)$ or perhaps they multiply: $\mathit{\Psi}(x,y,z)=\mathit{\Psi}_x(x)\cdot\mathit{\Psi}_y(y)\cdot\mathit{\Psi}_z(z)$? Instead of guessing, we can review some mathematical principles of differential equations to resolve between the two possibilities.

Separability is a method for solving differential equations, and what it means is that the Hamiltonian can be cast into a form whereby distinct terms that contain only an x, y or z are added or subtracted. A separable Hamiltonian is significantly easier to solve, and fortunately most (but not all) operators are in fact separable. To check for separability, first act on a wavefunction to the right of the Hamiltonian: $\hat{H}\mathit{\Psi}$ and then divide it out on the left: $\frac{1}{\mathit{\Psi}}\hat{H}\mathit{\Psi}$. What you are trying to see is if you can write out the Hamiltonian as:

\[\frac{1}

ParseError: invalid DekiScript (click for details)

_x\left(x\right)\cdot {\mathit{\Psi}}_y\left(y\right)\cdot {\mathit{\Psi}}_z\left(z\right)=\sim \left\{x\ terms\right\}+\left\{y\ terms\right\}+\left\{z\ terms\right\} \nonumber \]

and, if so, then the total wavefunction is: $\mathit{\Psi}(x,y,z)=\mathit{\Psi}_x(x)\cdot\mathit{\Psi}_y(y)\cdot\mathit{\Psi}_z(z)$.

Separability has two consequences. First, the wavefunction *cannot* look like $\mathit{\Psi}(x,y,z)\approx sin(k_x x+k_y y+k_z z)$ or $e^{i\cdot k_x\cdot x}+e^{i\cdot k_y\cdot y}+e^{i\cdot k_z\cdot z}$. Second, the method of separability gives us a way to solve the Schrödinger equation as each of the terms becomes a smaller and easier differential equation. Beginning with the definition of separability:

\[\frac{1}

ParseError: invalid DekiScript (click for details)

_x\left(x\right)\cdot {\mathit{\Psi}}_y\left(y\right)\cdot {\mathit{\Psi}}_z\left(z\right)= \nonumber \]

\[\frac{1}

ParseError: invalid DekiScript (click for details)

_x\left(x\right)\cdot {\mathit{\Psi}}_y\left(y\right)\cdot {\mathit{\Psi}}_z\left(z\right)+ \nonumber \]

$$\frac{1}{\mathit{\Psi}_x\left(x\right)\cdot \mathit{\Psi}_y\left(y\right)\cdot \mathit{\Psi}_z\left(z\right)}\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2}{\partial y^2}\mathit{\Psi}\left(x\right)\cdot \mathit{\Psi}\left(y\right)\cdot \mathit{\Psi}\left(z\right)+$$

\[\frac{1}

ParseError: invalid DekiScript (click for details)

_x\left(x\right)\cdot {\mathit{\Psi}}_y\left(y\right)\cdot {\mathit{\Psi}}_z\left(z\right) \nonumber \]

One simple rule of calculus is concerning derivatives is that functions of other variables are not “caught up” by the derivative operation, i.e. $\frac{\partial}{\partial x}f\left(x\right)f\left(y\right)=f\left(y\right)\frac{\partial f(x)}{\partial x}$. When we apply that to the 1^{st} term above we find:

\[\frac{1}

ParseError: invalid DekiScript (click for details)

_x\left(x\right)\cdot {\mathit{\Psi}}_y\left(y\right)\cdot {\mathit{\Psi}}_z\left(z\right)=\frac

ParseError: invalid DekiScript (click for details)

_x\left(x\right) \nonumber \]

which simplifies to $\frac{1}{\mathit{\Psi}_x(x)}\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\mathit{\Psi}(x)}{\partial x^2}$. Appling these across-the-board yields:

$$\left\{\frac{1}{\mathit{\Psi}_x\left(x\right)}\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\mathit{\Psi}_x\left(x\right)}{\partial x^2}\right\}+\left\{\frac{1}{\mathit{\Psi}_y\left(y\right)}\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\mathit{\Psi}_y\left(y\right)}{\partial y^2}\right\}+\left\{\frac{1}{\mathit{\Psi}_z\left(z\right)}\left(\frac{-\hbar^2}{2m}\right)\frac{\partial^2\mathit{\Psi}_z\left(z\right)}{\partial z^2}\right\}$$

Success! We see three distinct terms, whereby only an x appears in the 1^{st} one and so on. Furthermore, each term is now a min-Schrödinger equation to be solved. The last step is to realize that all three terms add up to the energy. You can see this starting with: $\hat{H}\mathit{\Psi}=E\mathit{\Psi}$ and dividing out the wavefunction on the left $\frac{1}{\mathit{\Psi}}\hat{H}\mathit{\Psi}=\frac{1}{\mathit{\Psi}}E\mathit{\Psi}=\frac{\mathit{\Psi}}{\mathit{\Psi}}E=E$. Since each term adds to a constant (the energy), then each term must be a constant in its own right. As a result, we divide the energy into three parts, one for x, for y and for z as: $E=E_x+E_y+E_z$, and then give each energy to the corresponding term (and using a little algebra to bring the wavefunctions to the right):

\[\left(\frac

ParseError: invalid Primary (click for details)

_x\left(x\right)=E_x{\mathit{\Psi}}_x\left(x\right) \nonumber \]

\[\left(\frac

ParseError: invalid Primary (click for details)

_y\left(y\right)=E_y{\mathit{\Psi}}_y\left(y\right) \nonumber \]

\[\left(\frac

ParseError: invalid Primary (click for details)

_z\left(z\right)=E_z{\mathit{\Psi}}_z\left(z\right) \nonumber \]

Each of these are simply freewave Schrödinger equations. We know from the last chapter that the solutions are: $\mathit{\Psi}_x\left(x\right)=e^{\pm i\cdot k_x\cdot x}$, etc., which means that the full solution is:

$$\mathit{\Psi}\left(x,y,z\right)=e^{\pm i\cdot k_x\cdot x}\cdot e^{\pm i\cdot k_y\cdot y}\cdot e^{\pm i\cdot k_z\cdot z}$$

It is interesting to note that three separate momentum components now add to the total like a vector: $k^2=k^2_x+k^2_z+k^2_z$. This is especially apparent if you use the wavefunction to calculate the total energy:

$$E=\frac{\hbar^2}{2m}\left(k^2_x+k^2_z+k^2_z\right)=\frac{\hbar^2k^2}{2m}$$

If for some reason the individual wavevectors were not of equal magnitude, then it would have to be true that the total energy wasn't divided equally between the three dimensions: $E_x\neq E_y\neq E_z$. This is a very unlikely scenario, but if it was true you would be aware of it due to the fact that you must have some basic understanding of the system under study. Or, if you are solving a problem this information would be given to you as an initial condition of the system.

14.1.2. The Particle in a 3D Box and Degeneracy

The quantum particle in a box can be extended to multiple dimensions as visually represented in Figure 14.1. From the last chapter, this problem was defined by a potential that is 0 inside the box and infinite outside. Boundary conditions allow us to define the wavefunctions: $\mathit{\Psi}=sin\left(\frac{n\pi}{L}x\right)$ with the quantum number n=1,2,3… that characterize the number of nodes and the energy. Extending this to multiple dimensions is straightforward. Given the previous discussion the total wavefunction is just the multiple of individual particle in a box functions for x, y and z:

$$\mathit{\Psi}_{2D}\left(x,y,z\right)=N_{2D}\cdot sin\left(k_xx\right)\cdot sin\left(k_yy\right)\ \mathit{\Psi}_{3D}\left(x,y,z\right)=N_{3D}\cdot sin\left(k_xx\right)\cdot sin\left(k_yy\right)\cdot sin\left(k_zz\right)$$

where the normalization constants are $N_{2D}=\frac{2}{\sqrt{L_xL_y}}$, $N_{3D}=\frac{2\sqrt{2}}{\sqrt{L_xL_yL_z}}$, and $k_x=\frac{n_x\pi}{L_x}$, $k_y=\frac{n_y\pi}{L_y}$, and $k_z=\frac{n_z\pi}{L_z}$. We will limit further discussion to the 3D case from here on. Inserting the wavefunction back into the particle in a box Hamiltonian reveals the energy to be:

$$E=\frac{\hbar^2}{2m}\left(k^2_x+k^2_y+k^2_z\right)=\frac{\hbar^2\pi^2}{2m}\left(\frac{n^2_x}{L^2_x}+\frac{n^2_y}{L^2_y}+\frac{n^2_z}{L^2_z}\right)$$

which can be simplified to $E=\frac{\hbar^2\pi^2}{2mL^2}\left(n^2_x+n^2_y+n^2_z\right)$ if all the box lengths are the same. As in the one-dimensional particle in a box problem, the quantum numbers are limited to whole numbers: $n_{x,y,z}=1,2,3\dots$ due to the need to satisfy boundary conditions imposed by infinite potential energies past the barriers. Various wavefunctions are depicted in Figure 14.2, where we have made the simplification that $L=L_x=L_y=L_z$. It can be seen that there is only one wavefunction that gives the lowest energy ground state for which $n_{x,y,z}=1$. However, there are three potential 1^{st} and 2^{nd} excited states; since for example:

$$E=\frac{\hbar^2\pi^2}{2m\cdot L^2}\left\{{\left(n_x=2\right)}^2+1^2+1^2\right\}=\frac{\hbar^2\pi^2}{2m\cdot L^2}\left\{1^2+{\left(n_y=2\right)}^2+1^2\right\}=\frac{\hbar^2\pi^2}{2m\cdot L^2}\left\{1^2+1^2+{\left(n_z=2\right)}^2\right\}$$

This is referred to as a degeneracy, multiple distinct states that all have the same energy. One way to recognize degeneracy is if you can rotate the wavefunctions such that they all look the same.

There isn't much more to say about these simple multidimensional systems. For example, one can generate interesting problems by mixing and matching potential surfaces in different dimensions- a freewave surface in x and a parabolic (spring) potential in y. However, the solutions are rather trivial, as the total wavefunction in this example is just the freewave in x times the harmonic oscillator function in y. Such problems are left for your effort at the end of the chapter, and as such we move on to discuss a quantum particle rotating.

14.2: Rotational Quantum Mechanics- Introduction

In chemistry, we are deeply concerned about electrons and how they can bunch up (bond), or not (antibond), between atomic nuclei; this is how molecules form. Unfortunately, atoms are round and their electrons may orbit the nucleus like the Moon rotates about the Earth. This means that electrons have angular momentum and rotational kinetic energy. We must use quantum mechanics to understand how rotation works for light particles such as electrons. Rotational quantum mechanics also applies to rotational spectroscopy of molecules, which is in the microwave region of the electromagnetic spectrum.

The most important thing about rotational energy is to determine the rotational kinetic energy operator. You may be thinking, “how is rotational kinetic energy different than translational kinetic energy?” This indeed sounds like a very difficult question; fortunately, the answer is that ***it isn’t different***. Meaning, the kinetic energy Hamiltonian we discussed above: $\frac{-\hbar^2}{2\cdot mass}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$, hasn’t changed at all! However, there is one slight problem- Cartesian coordinates are not very useful for round objects like atoms. Rather, we want to use either cylindrical or spherical coordinates. Thus, changing the kinetic energy operator from Cartesian (x, y, z) into cylindrical (r, ϕ, z) or spherical (r, ϕ, θ) coordinates is our first objective.

14.2.1 Cylindrical Coordinate Transformation

If you don’t recall how cylindrical and spherical coordinates work see the Example box on the next page. Once you are comfortable with these trigonometric equations, we can start on transforming the coordinate system by describing an object rotating exclusively in the x-y plane using cylindrical variables. This means that x, y $\rightarrow$ r, ϕ, while z remains z. Our first model is for a quantum mechanical particle that rotates in a flat x-y plane with a fixed radius; this is referred to as a 2D rigid rotor. Since the object does not move in the z direction we can leave the z coordinate out of the kinetic energy operator as so:

$$\hat{H}_{2D}=\frac{-\hbar^2}{2\cdot mass}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)$$

This simplifies our transformation problem. The first step is to use the product rule to relate $x\rightarrow r$ as follows:

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}$$

However, since x is a function of both r and ϕ we must include the ϕ dependency as well:

$$\frac{\partial}{\partial x}=\frac{\partial r}{\partial x}\frac{\partial}{\partial r}+\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}$$

Consequently, the transformation requires us to evaluate $\frac{\partial r}{\partial x}$ and $\frac{\partial\phi}{\partial x}$. Based on the relationships on the previous page, we see that $r=\sqrt{x^2+y^2}$ and thus:

\[\frac{\partial r}{\partial x}=\frac{\partial {\left(x^2+y^2\right)}^{\frac{1}{2}}}{\partial x}=\frac{1}{2}{\left(x^2+y^2\right)}^{-\frac{1}{2}}\cdot \frac{\partial x^2}{\partial x}=\frac{1}{2}\frac{2x}

ParseError: invalid DekiScript (click for details)

=\frac{x}

ParseError: invalid DekiScript (click for details)

\nonumber \]

Recall that we are not here to represent anything with x and y, rather r and ϕ. Thus, we must recognize that \(\frac{1}

ParseError: invalid DekiScript (click for details)

=\frac{1}{r}\) and \(x=r\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)). Putting this altogether we see:

\[\frac{\partial r}{\partial x}=\frac{x}

ParseError: invalid DekiScript (click for details)

=\frac{1}{r}r\cdot

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)\ =

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)\ \nonumber \]

Likewise, we evaluate $\frac{\partial\phi}{\partial x}$ as:

\frac{\partial \phi }{\partial x}=\frac{\partial atan(\frac{y}{x})}{\partial x}=-\frac{{{sin}}sinleft(\phi \right)\ }{r} \nonumber

Tying this all together reveals:

\[\frac{\partial }{\partial x}=

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)frac{\partial }{\partial r}-\frac{{{sin}}sinleft(\phi \right)\ }{r}\frac{\partial }{\partial \phi } \nonumber \]

A similar derivation for the y-coordinate reveals:

\[\frac{\partial }{\partial y}=

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(\phi \right)frac{\partial }{\partial r}+\frac{{{cos}}cosleft(\phi \right)\ }{r}\frac{\partial }{\partial \phi } \nonumber \]

The way to transform the kinetic energy operator is to evaluate $\frac{\partial^2}{\partial x^2}$ and $\frac{\partial^2}{\partial y^2}$ using the relationships above. The algebra involved isn't difficult but there are a very large number of steps; regardless, the end result is:

$$\hat{H} = \frac{-\hbar^2}{2\cdot mass}\cdot\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right) \rightarrow \frac{-\hbar^2}{2\cdot mass\cdot r^2}\cdot\frac{\partial^2}{\partial \phi^2}$$

14.2.2 2D rigid rotor

For this model problem, called the 2D rigid rotor, we assume that a light particle circulates on a flat potential in the x and y plane with a fixed z coordinate. The radius of the motion is fixed, so the particle travels around and around a completely flat track. We will begin by making an analogy to the particle in a box problem, which will allow us to introduce concepts important to rotation and to calculate the energy. To this end we create a visual representation of what the wavefunctions should look like by drawing the particle in a box states on a piece of paper as shown in Figure 14.4 A. There is one additional n = 0 state that has no kinetic energy; please note that the particle in a box doesn't have a n =0 state due to its zero-point energy. Next, we fold the paper over to see how each wavefunction bites its own tail as seen in Figure 14.4 B. Doing so allows us to see whether the wavefunction is smooth and continuous at the seam, for which we can that is the case for the n = 0 and n = 2 states. As a result, these are valid 2D rigid rotor wavefunctions. In contrast, the n = 1 and n = 3 are continuous but they are not smooth, and as such they are not valid 2D rigid rotor wavefunctions. If we analyze the other states we find that odd symmetry ones are ok, while the symmetric ones are not.

We can now calculate the de Broglie wavelength for the allowed states, which provides the momentum and thus the k vectors for the wavefunctions and allows us to calculate the energy. We can see from the figure that the allowed n=0 state has an infinite wavelength and that the n = 2 has a wavelength $\lambda = C$. We can assume that the other allowed states are n = 4 which has $\lambda = \frac{C}{2}$ and n = 6 for which $\lambda = \frac{C}{4}$. From here we can generate an empirical relationship: $\lambda = \frac{L}{m}$, where m = 0, 1, 2, … and appears to act like a quantum number. As it is not proper to express this wavelength as a function of the circumference of the track (C, same as the length of the particle in a box), rather its radius, for which we substitute $2\pi r = C$. We see that the wavelengths for allowed 2D rigid rotor states are: $\lambda = \frac{2\pi r}{m}$. The de Broglie momenta are then:

$$\frac{h}{\lambda} = \frac{hm}{2\pi r} = \frac{\hbar m}{r}$$

and the energy is momentum squared over mass:

$$E = \frac{\hbar^2 m^2}{2 \cdot mass \cdot r^2}$$

where $\hbar = \frac{h}{2\pi}$. Despite the unconventional approach we have taken the equation for energy above is correct and reveals the existence of a new quantum number “m” for 2D rotation. To finish out this section we introduce some terminology. We are describing is a component of orbital rotational angular momentum which is typically given the symbol “l_z”. It is important to note this here because later we will see that there is another quantity called the spin angular momentum that has to be added to calculate the total. Discussion on these topics are forthcoming; as it applies to the 2D rigid rotor and the energy of rotational motion is:

$$E = \frac{l_z^2}{2I}$$

where $I = mass \cdot r^2$ and is called the moment of inertia. From the analogy to the equation for energy above we can see that $l_z = \hbar m$, and thus rotational momenta are quantized due to the need for the wavefunction to “bite its tail”, i.e. be smooth and continuous.

14.2.2.1 2D Rigid Rotor Wavefunctions

The above is a fine start to demonstrate the principles of rotational quantum mechanics; however here we will employ more rigorous mathematics. We first find the wavefunctions which can be used to calculate the energies and evaluate other properties. This is accomplished by defining the angular momentum operator:

$$\hat{L}_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$$

which makes potential-free Hamiltonian:$\hat{H} = \frac{\hat{L}_z^2}{2I} = \frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$. Now the eigenvalue (Schrödinger) equation can be defined as:

$$\frac{-\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2} \Psi(\phi) = E \cdot \Psi(\phi)$$

where, as before, I is the moment of inertia. The wavefunction solution to the above is:

$$e^{i \cdot m \cdot \phi}$$

where “m” is a constant that must be determined using boundary conditions. As you recall the same approach allowed us to determine all the details of the particle in a box. Concerning boundary conditions, we can see from Figure 14.4 B that the wavefunctions must be continuous at the “seam”, which is defined where $\phi = 0$ meets $\phi = 2\pi$. Thus, $\Psi(\phi) = \Psi(\phi + 2\pi)$, which when applied to the wavefunction:

$$e^{i \cdot m \cdot (\phi + 0)} = e^{i \cdot m \cdot (\phi + 2\pi)} = e^{i \cdot m \cdot \phi} e^{i \cdot m \cdot 2\pi}$$

This only works if $e^{i \cdot m \cdot 2\pi} = 1$, which means that $m = dots, -2, -1, 0, 1, 2, \ldots$ using identities for complex exponentials. As before, we have a new integer quantum number defined in exactly the same way as was found using our earlier approach to explore the 2D rigid rotor. One difference between the m quantum number and earlier examples is that it can be negative. This actually has a simple meaning; a positive m is for a quantum particle rotating clockwise while a negative value is for a particle rotating counterclockwise. If the 2D rigid rotor decides not to rotate at all, then m=0.

The rotational energy is:

$$\frac{\hat{L}_z^2}{2I}\Psi(\phi) = \frac{-\hbar^2}{2I}\frac{\partial^2}{\partial\phi^2}\Psi(\phi) = \frac{\hbar^2 m^2}{2I}\cdot\Psi(\phi)$$

and is exactly the same result derived previously. As usual we should normalize the state(s) via:

$$\int_0^{2\pi} N^2\cdot e^{-i\cdot m\cdot\phi}\cdot e^{i\cdot m\cdot\phi}\partial\phi = N^2\cdot\phi]_0^{2\pi} = N^2 2\pi = 1$$

which reveals that the proper normalized wavefunction is:

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}}e^{i\cdot m\cdot\phi}$$

There isn't much more to say about this rather simple introduction to rotation, and as such we now move onto a particle that isn't trapped in the x-y plane as discussed below. Before we do so, you should know that you will see the 2D rigid rotor once more when the wavefunctions for the hydrogen atom are calculated. In fact, this is where we get our notion for p$_x$, p$_y$ and p$_z$ orbitals; these are revealed in Ch. 15.

14.2.3 The 3D rigid rotor

For exploring rotational motion in three dimensions we will create the most simple model possible by stating that a quantum particle rotates with a fixed radius on a 3D track that has no potential energy. As with the 2D case we first develop the kinetic energy operator. To this end we convert coordinates $x, y, z \rightarrow r, \phi, \theta$ step by step beginning with:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi} + \frac{\partial\theta}{\partial x}\frac{\partial}{\partial\theta}$$

and then the same for $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$. With these worked out we can then convert the kinetic energy operator into the same using spherical coordinates. Unfortunately, the algebra to do so is extraordinarily tedious and as a result we will simply provide the end result here:

$$\hat{H} = \frac{-\hbar^2}{2\cdot mass}\cdot\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) \rightarrow \frac{-\hbar^2}{2I}\cdot\left(\frac{1}{sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{sin(\theta)}\frac{\partial}{\partial\theta}sin(\theta)\frac{\partial}{\partial\theta}\right)$$

where the moment of inertial is defined as before: $I = mass\cdot r^2$. The above Hamiltonian is usually simplified as: $\hat{H} = \frac{\hat{L}^2}{2I}$, where $\hat{L}$ is the total (3D) orbital angular momentum operator. Regardless of the notation, the Hamiltonian in spherical coordinates appears pretty fearsome and there isn't much we can do about that other than to begin to solve it using the method of separability. First, we assume that the solution has the form:

$$\psi(\phi,\theta) = \psi(\phi)\psi(\theta)$$

This separated wavefunction is applied to the Hamiltonian: $\hat{H}psi(\phi)\psi(\theta)$:

\[\frac

ParseError: invalid Primary (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\right)\psi \left(\phi \right)\psi \left(\theta \right)=E\cdot \psi \left(\phi \right)\psi \left(\theta \right) \nonumber \]

Moving the constants to right side makes this look a little easier:

\[\left(\frac{1}

ParseError: EOF expected (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\right)\psi \left(\phi \right)\psi \left(\theta \right)=\frac{-2I\cdot E}{\hslash^2}\cdot \psi \left(\phi \right)\psi \left(\theta \right) \nonumber \]

And now we divide out the wavefunction on the left side:

\[\frac{1}{\psi \left(\phi \right)\psi \left(\theta \right)}\left(\frac{1}

ParseError: EOF expected (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\right)\psi \left(\phi \right)\psi \left(\theta \right)=\frac{1}{\psi \left(\phi \right)\psi \left(\theta \right)}\frac{-2I\cdot E}{\hslash^2}\cdot \psi \left(\phi \right)\psi \left(\theta \right) \nonumber \]

If you are slow and methodical you find that the process of solving the above is fairly straightforward. For example, the $\frac{\partial}{\partial\theta}$ derivative captures $\psi\left(\theta\right)$ yet allows $\psi\left(\phi\right)$ to pass through (and vice versa); after some algebra we see that:

\[\frac{1}{\psi \left(\phi \right)\cdot {sin}^2\left(\theta \right)}\frac

ParseError: invalid DekiScript (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\psi \left(\theta \right)=\frac{-2I\cdot E}{\hslash^2} \nonumber \]

At this point there is a problem with separation because the first part:

$$\frac{1}{\psi\left(\phi\right)\cdot sin^2\left(\theta\right)}\frac{\partial^2}{\partial\phi^2}\psi\left(\phi\right)$$

containing mostly ϕ terms but also has a pesky $\frac{1}{sin^2(\theta)}$ term. To remove the problem we multiply everything by $sin^2\left(\theta\right)$:

\[\frac{1}{\psi \left(\phi \right)}\frac

ParseError: invalid DekiScript (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\psi \left(\theta \right)=\frac{-2I\cdot E}{\hslash^2}{sin}^2\left(\theta \right) \nonumber \]

Now we have a clean separation of ϕ and$theta$ terms into mini-Schrödinger equations, although it is interesting to note that the energy is on the θ side:

\[\left(\frac{1}{\psi \left(\phi \right)}\frac

ParseError: invalid DekiScript (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\psi \left(\theta \right)+\frac{2I\cdot E}{\hslash^2}{sin}^2\left(\theta \right)\right)=0 \nonumber \]

To solve this, we assume that the solution to the ϕ mini-Schrödinger equation (left side) is the same as the 2D rigid rotor that we worked on previously: $\psi\left(\phi\right)=\frac{1}{\sqrt{2\pi}}e^{i\cdot m\cdot\phi}$. As a result:

$$\frac{1}{\psi\left(\phi\right)}\frac{\partial^2}{\partial\phi^2}\psi\left(\phi\right)=\sqrt{2\pi}\cdot e^{-i\cdot m\cdot\phi}\frac{\partial^2}{\partial\phi^2}\frac{1}{\sqrt{2\pi}}e^{i\cdot m\cdot\phi}=-m^2$$

which when inserted into the full equation above we find that:

\[\frac

ParseError: colon expected (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\psi \left(\theta \right)+\frac{2I\cdot E}{\hslash^2}{sin}^2\left(\theta \right)=m^2 \nonumber \]

”One of the most interesting aspects of quantum mechanics is that this differential equation was solved in 1782 by Pierre Simon de Laplace, who was called the “Newton of France” and was one of Napoleon Bonaparte’s teachers. The solutions are called the spherical harmonics and are listed in Table 14.1. The wavefunctions are classified by a new quantum number l, which as usual can only have integer values: $l = 0,\ 1,\ 2,\ 3\ldots$. There are $2l+1$ wavefunctions associated with each l quantum number, which are due to the 2D rigid rotor m quantum number that will now be abbreviated as m_l. They can take on integer values $m_l = l, (\,l-1), \ldots 0 \cdots -l$, and it is important to note that there are $2l+1$ possibilities. The wavefunctions are thus abbreviated as Y_{l,m_l} to designate the l and sub-m_l quantum states. Now that we know the wavefunctions we can use the to calculate the total orbital angular momentum using the $\hat{L}^2$ operator, which returns a function based on the l quantum number:

$$\hat{L}^2 Y_{l,m_l} = l\,(l+1)\,\hbar^2 \cdot Y_{l,m_l}$$

This allows to calculate the energy of the 3D rigid rotor:

$$E = l\,(l+1)\,\frac{\hbar^2}{2mr^2} = l\,(l+1)\,\frac{\hbar^2}{2I}$$

which are $2l+1$ degenerate as discussed above.

The spherical harmonics are important to a very large number of scientific fields and are often abbreviated as $Y_{l,m_l}(\phi, \theta)$. We will now examine them as a function of the l quantum number, which may look surprisingly similar to the wavefunctions you learned about for the hydrogen atom in Freshman chemistry.

14.3: Wavefunctions

Laplace's wavefunctions are probably familiar to most physical chemistry students already. For example, the lowest energy solution $l=0$, $m_l=0$ has the solution:$Y_{l=0,\, m_l=0}\left(\phi,\theta\right)=\frac{1}{\sqrt{4\pi}}$

This lowest energy state is referred to as the s-state and it has no dependence on angle. To plot this wavefunction we will use what is called a "probability isosurface", which is a picture of where all the probabilities $\left|Y_{l,m_l}\left(\phi,\theta\right)\right|^2$ have a specific value, such as $\left|Y_{l,m_l}\left(\phi,\theta\right)\right|^2=0.95$. When applied to $Y_{0,0}$ we see a sphere as shown in Figure 14.5. What is interesting to note is that, while it is intuitive to describe a particle with a wavefunction as clearly circulating the origin this is in fact not the case as the rotational energy is:

$$E=l\left(l+1\right)\frac{\hbar^2}{2I}=0\ J$$

The proper way to see this fact is that the wavefunction has no nodes, which is how quantum mechanics always imparts kinetic energy including rotational.

14.3.1. P- and d-states. Now let's climb the rotational kinetic energy ladder and examine the p-states. There must be three $l=1$ wavefunctions given the m_l level degeneracy ($m_l=-1,0,1$), and they are plotted in Figure 14.6. We expect that we may see hydrogen-like p_z, p_x and p_y states, and in fact the $m_l=0$ sure looks like p_z! However, the two $m_l=\pm1$ wavefunctions do not look anything like p_x or p_y!

The reason why you aren't seeing the expected p_x and p_y "dumbbells" is that the spherical harmonics with finite values of the m quantum number have $e^{\pm i\cdot m\cdot\phi}$ terms, which are complex (i.e. it contains real and imaginary numbers). Such functions are travelling waves; however, we would prefer stationary waves if possible. It turns out that we can remove the travelling wave components simply by making linear combinations of the spherical harmonics, which is valid because the sum of two Hamiltonian wavefunctions is still a valid wavefunction.

In this endeavor, let's see what happens if we do this: $Y_{1,1}+Y_{1,-1}$, which is an attempt to remove the m_l dependence. Looking up the functions from the table yields:

$$Y_{1,1}+Y_{1,-1}=\sqrt{\frac{3}{8\pi}}sin\left(\theta\right)e^{i\cdot\phi}+\sqrt{\frac{3}{8\pi}}sin\left(\theta\right)e^{-i\cdot\phi}$$

Next, collecting terms and using the identity $e^{-i\cdot\phi}+e^{i\cdot\phi}sim\ cos(\phi)$ yields:

$$Y_{1,-1}+Y_{1,1}sim\ sin\left(\theta\right)cos\left(\phi\right)$$

If we recall that, for spherical coordinates: $x=sin\left(\theta\right)cos\left(\phi\right)$, which makes $Y_{1,1}+Y_{1,-1}$ equal to the p_x orbital. Following the same idea we find that the difference of the two spherical harmonics $Y_{1,1}-Y_{1,-1}$ can be simplified using $e^{i\cdot\phi}-e^{-i\cdot\phi}sim\ sin(\phi)$ to:

$$Y_{1,1}-Y_{1,-1}\sim sin\left(\theta\right)sin\left(\phi\right)$$

and since $y=sin\left(\theta\right)sin\left(\phi\right)$ then \(Y_{1,1}+Y_{1,-1})is the p_y orbital. In fact, when we plot the isosurfaces of these functions in Figure 14.7 we see that is indeed the case.

Running through the same arguments for the five $l=2$ d-states yields familiar hydrogen-like results as shown in Figure 14.8, and similarly for the seven f states. We will see these functions again when studying the hydrogen atom in the next chapter. Furthermore, the periodic table is arranged based on the l quantum number. Hopefully you learned in Freshman chemistry that $l=1$ is the main block, $l=2$ are for the transition metals and $l=3$ are the trans-uranium elements.

14.4: Spin Angular Momentum

You should recall from your many other classes that electrons are “spin one-half” and can either be spin up or spin down. You applied these facts when creating the electron configuration of transition metals in your inorganic chemistry class; an example for the 16-electron tetrahedral compound nickel carbonyl is shown in Figure 14.9. Why only spin up or down? Because, if the angular momentum of an electron is $l = \frac{1}{2}$, then the allowed m_l values are $+\frac{1}{2}$ and $-\frac{1}{2}$. More important is to understand what spin angular momentum is. While it is tempting to state that the electron is spinning on its axis like the earth, akin to the type of angular motion that was discussed in the previous sections, unfortunately this is not the case. The reason is that there are many other subatomic particles that have the same half spin momentum, including the proton, neutron, and quarks. Given that “normal” angular momentum is proportional to mass, and a proton is $\sim$2000$\times$ heavier than an electron, how could they possibly have the exact same spin from classical rotational motion? The conclusion is that spin is a type of angular momemtnum, but it doesn’t originate from the type of rotational motion that we are accumtomed to.

Unfortunately no one really knows what spin angular momentum is other than its existence can be demonstrated by integrating Einstein’s theory of relativity with quantum mechanics. As a result, it is considered important to distinguish spin angular momentum from “normal” orbital angular momentum discussed here. To do so, spin angular momentum is designated with “s” as the quantum number (similar to l for orbital angular momentum). There is a spin angular momentum operator $\hat{S}$ that, when applied to the spin wavefunction $\psi = \alpha$ or $\psi = \beta$ yields:

$$\hat{S}^2 \alpha = s(s+1)\hbar^2 \cdot \alpha$$

likewise $\hat{S}^2 \beta = s(s+1)\hbar^2 \cdot \beta$. Thus, the total angular momentum is $\sqrt{s(s+1)}\,\hbar = \sqrt{\frac{3}{4}}\hbar$ for either the α or β state. There are sub-m_S states designated with the s_z quantum number, which is known as the “magnetic spin”. This name comes about because the magnetic properties of electrons are due to spin, which is the source of the magnetism used in power plant turbine electrical generators. The magnetic spin operator $\hat{S}_z$ has the following properties when applied to the spin α and β wavefunctions:

$$\hat{S}_z \alpha = s_z \cdot \alpha = ½\hbar \cdot \alpha and\ \hat{S}_z \beta = s_z \cdot \beta = -½\hbar \cdot \beta$$

which allows us to distinguish them. The names “up” for α and “down” for β came about because, if you accelerate an electron in a magnetic field, you will see the electrons either deflect upwards or downwards depending on the magnetic spin quantum number. Spin is also the source of magnetism of protons and neutrons that makes certain elements and isotopes NMR active. This type of nuclear magnetism is however much weaker than the fields created by electrons.

The wavefunctions are orthonormal: $\int \alpha^* \alpha = \int \beta^* \beta = 1$ while $\int \alpha\beta = 0$, which is important when we discuss the hydrogen atom next chapter. At this point you are probably expecting to see some kind of function for the α and β states, maybe a complex exponential or a sine or cosine; however, we don’t really know what spin is so there is no mathematical definition for it as a result. What the spin wavefunctions allow us to do is to satisfy the Pauli principle, which you may recall is why you fill atomic orbitals with spin up electrons first and then spin down. The Pauli principle states that no two electrons can be in the same state at the same time, and the fact that electrons have spin is why you can have two occupy the same atomic orbital but not violate that rule at the same time.

14.5: Angular Momentum Operators

Angular momentum is defined as:

$$L\rightharpoonup = r\rightharpoonup \times p\rightharpoonup$$

where $r\rightharpoonup$ is the position of the particle, $p\rightharpoonup$ is momentum and reveals the direction of motion, and $L\rightharpoonup$ is the angular momentum vector. As everything is a vector the angular momentum can be decomposed into x, y and z components, i.e. $L\rightharpoonup = \hat{L}_x + \hat{L}_y + \hat{L}_z$ (this will be important later). While understanding angular momentum can be intimidating, if you look at Figure 14.10 you see that it is basically the axel of a wheel as defined by the rotation of a particle. As shown in the figure the only nuance is that the right-hand rule dictates whether the vector is up or down depending on the direction that the particle is rotating. The relationship $L\rightharpoonup = r\rightharpoonup \times p\rightharpoonup$ was part of your learning of classical mechanics; likely you learned about it Physics I or even in high school. To create a quantum mechanical operator for angular momentum, we simply insert $\hat{r}$ as the position operator and $\hat{p} = \frac{\hbar}{i}\left\{\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}\right\}$ as the momentum operator into $r \times p$. The cross product simplifies into relationships for angular momentum as projected into x, y and z as:

$\hat{L}_x = \frac{\hbar}{i}\left\{y\cdot\frac{\partial}{\partial z} - z\cdot\frac{\partial}{\partial y}\right\}$, $\hat{L}_y = \frac{\hbar}{i}\left\{z\cdot\frac{\partial}{\partial x} - x\cdot\frac{\partial}{\partial z}\right\}$, and $\hat{L}_z = \frac{\hbar}{i}\left\{x\cdot\frac{\partial}{\partial y} - y\cdot\frac{\partial}{\partial x}\right\}$

Next, we insert x, y, and z in spherical coordinates. You may recall we already showed how to covert $\frac{\partial}{\partial x}$ etc.: $\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta}$ and likewise: $\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta}$. These simplify to:

\[\frac{\partial }{\partial x}=sin\left(\theta \right)

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)\frac{\partial }{\partial r}\ +\frac{cos\left(\theta \right)cos\left(\phi \right)}{r}\frac{\partial }{\partial \theta }-\frac{sin\left(\phi \right)}{r\cdot sin\left(\theta \right)}\frac{\partial }{\partial \phi } \nonumber \]

and:

\[\frac{\partial }{\partial y}=sin\left(\theta \right)

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(\phi \right)\frac{\partial }{\partial r}\ +\frac{cos\left(\theta \right)sin\left(\phi \right)}{r}\frac{\partial }{\partial \theta }+\frac{cos\left(\phi \right)}{r\cdot sin\left(\theta \right)}\frac{\partial }{\partial \phi } \nonumber \]

Hence the angular momentum in the z direction is: $\hat{L}_z = \frac{\hbar}{i}\left\{x\cdot\frac{\partial}{\partial y} - y\cdot\frac{\partial}{\partial x}\right\} = \frac{\hbar}{i}\bullet$

\[\{r\cdot sin\left(\theta \right)cos\left(\phi \right)\cdot sin\left(\theta \right)

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(\phi \right)\frac{\partial }{\partial r}\ +r\cdot sin\left(\theta \right)cos\left(\phi \right)\cdot \frac{cos\left(\theta \right)sin\left(\phi \right)}{r}\frac{\partial }{\partial \theta }+r\cdot sin\left(\theta \right)cos\left(\phi \right)\cdot \frac{cos\left(\phi \right)}{r\cdot sin\left(\theta \right)}\frac{\partial }{\partial \phi }\ -r\cdot sin\left(\theta \right)sin\left(\phi \right)\cdot sin\left(\theta \right)

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)\frac{\partial }{\partial r}\ -r\cdot sin\left(\theta \right)sin\left(\phi \right)\cdot \frac{cos\left(\theta \right)

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)\ }{r}\frac{\partial }{\partial \theta }+r\cdot sin\left(\theta \right)sin\left(\phi \right)\cdot \frac{sin\left(\phi \right)}{r\cdot sin\left(\theta \right)}\frac{\partial }{\partial \phi }\}\ \nonumber \]

While this looks overwhelming, note how the first two terms on each line cancel, leaving:

$$\hat{L}_z=\frac{\hbar}{i}\cdot\left\{r\cdot sin\left(\theta\right)cos\left(\phi\right)\cdot\frac{cos\left(\phi\right)}{r\cdot sin\left(\theta\right)}+r\cdot sin\left(\theta\right)sin\left(\phi\right)\cdot\frac{sin\left(\phi\right)}{r\cdot sin\left(\theta\right)}\right\}\frac{\partial}{\partial\phi}=$$

$$\frac{\hbar}{i}\cdot\left\{cos^2\left(\phi\right)+sin^2\left(\phi\right)\right\}\frac{\partial}{\partial\phi}=\frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Very simple! Along the same lines you find that:

\[{\hat{L}}_x=\frac\hslash{i}\left(-

UndefinedNameError: reference to undefined name 'cot' (click for details)

cotleft(\theta \right)\

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)frac{\partial }{\partial \phi }-

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(\phi \right)frac{\partial }{\partial \theta }\right) \nonumber \]

and:

\[{\hat{L}}_y=\frac\hslash{i}\left(-

UndefinedNameError: reference to undefined name 'cot' (click for details)

cotleft(\theta \right)\

UndefinedNameError: reference to undefined name 'sin' (click for details)

sinleft(\phi \right)frac{\partial }{\partial \phi }+

UndefinedNameError: reference to undefined name 'cos' (click for details)

cosleft(\phi \right)frac{\partial }{\partial \theta }\right) \nonumber \]

The angular kinetic energy can be derived from:

$$\frac{\hat{L}^2}{2I}=\frac{\left(\hat{L}_x+\hat{L}_y+\hat{L}_z\right)^2}{2I}=\frac{-\hbar^2}{2I}\left(\frac{1}{sin^2\left(\theta\right)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{sin(\theta)}\frac{\partial}{\partial\theta}sin(\theta)\frac{\partial}{\partial\theta}\right)$$

which is exactly the same as shown before.

Overall is it unfortunate that all these operators are a bit complicated, but they are important because they reveal the existence of another uncertainty principle. You may recall from Ch. 13 section that, for two operators $\hat{A}$ and $\hat{B}$ if the following is true: $\left[\hat{A},\hat{B}\right]=\hat{A}\cdot\hat{B}-\hat{B}\cdot\hat{A}\neq 0$

(the operators don't commute), then the two operators don't share the same eigenvectors. In other words, if $\mathit{\Phi}$ is an eigenvector of $\hat{A}$, then $\hat{A}\mathit{\Phi}=\omega\mathit{\Phi}$ where ω is just a constant such as $\hbar$ or 0. However, the eigenvalue equation for won't work for the other operator: $\hat{B}\mathit{\Phi}\neq\omega\mathit{\Phi}$. Hence, whatever observable that $\hat{B}$ describes, you can't know what that is for the state described by $\mathit{\Phi}$. For example, in the previous chapter it was shown that $[\hat{x},\hat{p}]=-i\hbar$ for operators $\hat{x}$ and $\hat{p}$, so you can't know where something is and where it is going fully at the same time.

Returning to our rotational wavefunctions (the spherical harmonics), these have to be eigenfunctions of the $\hat{L}^2$ operator because they were solved to be the wavefunctions of rotational kinetic energy which is just $\hat{L}^2$ times a constant. Since it is always true that an operator commutes with its square, i.e. $\left[\hat{L}^2,\hat{L}\right]=\hat{L}^2\hat{L}-\hat{L}\hat{L}^2=\hat{L}^3-\hat{L}^3=0$, then the spherical harmonics are all eigenfunctions of $\hat{L}$. If you apply $\hat{L}_z$, you see that all of the spherical harmonics are eigenfunctions of $\hat{L}_z$ too. Since $\hat{L}$ and $\hat{L}_z$ share a common set of eigenfunctions, then it must be true that $\left[\hat{L},\hat{L}_z\right]=0$. However, using the operators above you can show that: $\left[\hat{L},\hat{L}_x\right]\neq 0$, $\left[\hat{L},\hat{L}_y\right]\neq 0$, $\left[\hat{L}_z,\hat{L}_x\right]\neq 0$, and finally $\left[\hat{L}_z,\hat{L}_y\right]\neq 0$. Hence, when describing rotation we can know the total angular momentum $\langle\hat{L}\rangle$ (the length of the "axel" in Figure 14.9) and the projection onto the z-axis $\langle\hat{L}_z\rangle$ (the tilt of the angular momentum vector), but we don't know the projection of angular momentum onto the x or y axes, i.e. $\langle\hat{L}_x\rangle$ and $\langle\hat{L}_y\rangle$. This is represented in Figure 14.11, where the motion of the quantum particle is displaced from the origin of its angular momentum vector so you can more easily see the rotation. What it means for $\langle\hat{L}_x\rangle$ and $\langle\hat{L}_y\rangle$ to be unknown is that the ϕ angle of the angular momentum vector is not defined. As a result, the angular momentum vector $\langle\hat{L}\rangle$ can point anywhere in the x-y plane when $m_l=0$. If $m_l=1$, the angular momentum vector can be anywhere on the surface of a cone as shown to the right of Figure 14.11. The cone representation on the right also includes $m_l=-1$; examples for $l=\frac{1}{2}$ and $l=2$ are also provided in Figure 14.12 where again we emphasize that the L vectors lie on the surface of the cones, yet they describe rotation about those vectors like a wheel about its axel.

14.6: Addition of Angular Momentum and Term Symbols

One of the more complicated things about electronic structure is the addition of spin and "normal" orbital angular momenta. This is important because the total energy is proportional to the square of the total angular momentum. Thus far we have already introduced $\hat{L}$ and $\hat{S}$ operators and their associated l and s quantum numbers as defined previously. Now we define the total angular momentum operator $\hat{J}$:

$$\hat{J} = \hat{L} + \hat{S}$$

A pictorial representation is shown in Figure 14.13. The total angular momentum operator returns eigenvalues via:

$$\hat{J}\psi = \hbar\sqrt{j(j+1)} \cdot \psi$$

where j is the quantum number for the total angular momentum, and likewise there are sub-total angular momentum states determined by the operator $\hat{J}_z$ that has eigenvalues j_z. Similar to the m_l quantum numbers, the allowed values for j_z are:

$$j,\ j-1\ldots 0\cdots -j$$

The wavefunctions of the total angular momentum operators $\hat{J}$ and $\hat{J}_z$ are sums of the individual orbital×spin states.

An atom with both orbital (l) and spin (s) momentum angular momenta is like a gyroscope that has another gyroscope on top of it. While this sounds complicated, to sum the momentum one simply uses vector addition. However, there is a problem when it comes to quantum angular momenta because the uncertainty principle dictates that the x, y and z components of either the orbital l or spin s momentum vectors are not fully known. Furthermore, we aren't so concerned with $\hat{J}$, rather $\hat{J}^2$ as the square of the momentum gives us the energy. Fortunately, the mathematics of connecting the l orbital and s spin together to form j have been established; however this is best left to graduate-level texts on quantum mechanics. Here we will show the end result, which is that the final j quantum number results from either constructive (addition) or destructive (subtraction) of the l and s angular momenta, which when applied to the quantum numbers results in the following relationship:

$$j = l+s,\ l+s-1\ldots |l-s|$$

Take for example a hydrogen atom in a $2p^1$ excited state. Here, we have to add the spin angular momentum $s = \frac{1}{2}$ with the orbital momentum $l = 1$. As a result, we can see that there are two possible j states: $j = l+s = 1+\frac{1}{2} = \frac{3}{2}$ and $j = l-s = 1-\frac{1}{2} = \frac{1}{2}$. We can express this information in a quantity called a term symbol: ${}^{2S+1}\mathrm{L}_j$; in this example there are two possible states labeled ${}^2P_{\frac{3}{2}}$ and ${}^2P_{\frac{1}{2}}$. It is important to note that there are six possible states for the $2p^1$ electron configuration because there are two possible spins (up or down) that can go into one of three orbitals (p_x, p_y and p_z); these are depicted in Figure 14.14. As a result, there must also be six j states, and we can find them once we consider the sub-total angular momentum states j_z.

For $j = \frac{3}{2}$ there are four sub-states $\left(j_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\right)$, while $j = \frac{1}{2}$ has two sub-states $\left(j_z = \frac{1}{2}, -\frac{1}{2}\right)$ for a total of six. It is important that we don't "lose" states when adding them together! These states are shown to the right of Figure 14.14, where you can see that the different j states are linear combinations of the singularly filled p_x, p_y and p_z orbitals. Last, we note that these states are degenerate, however there is an effect called spin orbit coupling that energetically favors the ${}^2P_{\frac{1}{2}}$; this is explained in the next chapter.

You might be curious about the 2S+1 part of the term symbol. This is called the multiplicity, and to explain it let's do another example of the addition of angular momentum just for spin. We run into such a problem for the excited state of helium with an electron configuration of $1s^1 2s^1$ as shown in Figure 14.15. As there is no l angular momentum, we are simply adding the two s quantum numbers, s_1 and s_2 to the total angular momentum that we call s_{tot}. Following the addition rules reveals two possibilities, one of which is: $s_{tot} = s_1 + s_2 = \frac{1}{2} + \frac{1}{2} = 1$. This configuration must have a total of three sub-s_{tot} states which are:

$$s_{tot},\ s_{tot}-1, -s_{tot} = 1,\ 0, -1$$

You may have figured out already based on the diagram that these are the triplet states, where $\uparrow\uparrow$ is for the +1 sub-s_{tot} state, $\downarrow\downarrow$ is for -1 and $\uparrow\downarrow + \downarrow\uparrow$ is for 0. Likewise there is the singlet state with a $s_{tot} = s_1 - s_2 = 0$, which has the associated spin wavefunction $\uparrow\downarrow - \downarrow\uparrow$. The singlet state cannot be degenerate. Consequently, the 2S+1 part of a term symbol is meant to convey the degeneracy expected due to spin angular momentum.

CHAPTER OVERVIEW

15: The Hydrogen Atom

The last chapters introduced you to quantum mechanical fundamentals starting from the de Broglie hypothesis. You learned about eigenvalue equations, operators and wavefunctions, and you tackled harder subjects like multidimensional Hamiltonians and rotational motion. Most important, the mathematics of probability and statistics have been shown to be essential for our interpretation of quantum mechanical principles. It is ironic that we wrap up this part of our learning exactly where Schrödinger began; he introduced the world to quantum mechanics by solving the energy levels of the hydrogen atom in the 1926 paper “Quantization as an Eigenvalue Problem.” In it, the electron is described with a wavefunction that is centered over a stationary nucleus. And while there are plenty of quantum problems beyond the hydrogen atom, this is the last “pen-and-paper” example that we can solve for reasons you will see at the end of this chapter.

We begin with a historical note on the first explorations on the electronic structure of hydrogen starting with Johann Balmer in 1855. At this time it was known that excited hydrogen emits light over a few discrete wavelengths as shown in Figure 15.1A. Balmer and Johannes Rydberg demonstrated that the emission can be described by the equation:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where λ is the emission wavelength, n_1 and n_2 are whole numbers, and $R = 1.097 \times 10^7\ m^{-1}$ is a constant named after Rydberg. This introduces the question, why would discrete emissions be observed, and what model for the hydrogen atom would have atomic energy levels that scale according to the square of a whole number? One of the first attempts to model hydrogen that correctly predicted this behavior was developed by Niels Bohr (Nobel Prize, 1922) as discussed below. This attempt also reveals another aspect of science, which is that a scientific theory is either everything or it is nothing.

Reference

1. L. M. Haffner *et al* 2003 *ApJS* **149** 405.

15.1: The Bohr Model

In 1913 Niels Bohr proposed a model for the hydrogen atom where the electron only exists in certain regions of space as it circulates around the nucleus (a single proton) as cartoonishly depicted in Figure 15.1B. He partially incorporated quantum theory by assumed that the orbiting electron can only have discrete values for the angular momentum. To model this behavior the angular momentum ($mv \cdot r$) was assumed to take integer values of $\hbar$, which is the reduced Planck constant (h/2π):

$$mv \cdot r = n \cdot \hbar$$

where n=1, 2, 3, etc. This means that velocity must be quantized: $v = \frac{n\hbar}{m \cdot r}$. Next, Bohr conjectured that the "outward" centripetal force: $\frac{mv^2}{r}$ matches the "inward" Coulomb attraction force:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

According to the above $v = \sqrt{\frac{e^2}{4\pi\varepsilon_0 \cdot m \cdot r}}$, which must be equal to our previous expression velocity:

$$\frac{n\hbar}{m \cdot r} = \sqrt{\frac{e^2}{4\pi\varepsilon_0 \cdot m \cdot r}}$$

This allows us to solve for the electron's radius: $r = \frac{4\pi\varepsilon_0 \cdot n^2\hbar^2}{m \cdot e^2}$, which is a function of the integer n. If n = 1 the radius is: $r = \frac{4\pi\varepsilon_0\hbar^2}{m \cdot e^2}$, which is the famous Bohr unit of length a_0 = 0.053×10^{-9} m.

The energy can be calculated by adding the kinetic and potential from the electrostatic attraction: $\frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$, where the Coulomb energy is negative since the electron and proton have opposite charges. Since both velocity and radius are quantized, Bohr was able to show that the same is true for the energy levels:

$$E = -\frac{e^4 m}{32\pi^2\varepsilon_0^2 \cdot \hbar^2} \cdot \frac{1}{n^2}$$

Inserting n = 1 gives the ground state energy: $-\frac{m \cdot e^4}{32\pi^2\varepsilon_0^2 \cdot \hbar^2} = -13.6\ eV$, which reveals how much energy has to be injected into the atom to fully remove the electron from the proton. And while this is the same value as measured experimentally, there are two problems with the model. For one, it doesn't explain the experimental observations that the spectra change under an applied magnetic field. Also, the model only works for atoms with one electron. More importantly, if an electron is circulating about a fixed point then it should emit electromagnetic waves; this is how a microwave oven heats your leftovers. If so, the electron eventually loses all its energy and crashes into the nucleus, and poof no more atom! Obviously, this doesn't happen. Consequently, the Bohr model was rejected which brings us to 1926 when Schrödinger formulated the hydrogen atom's Hamiltonian and used an eigenvalue equation approach to solve it.

15.2: The Hydrogen Schrödinger Equation

Concerning the energy of an atom, even a simple one as hydrogen, we must solve the wavefunction for both the electron and the proton. Afterall, light particle including protons may need to be described with wavefunctions. Electron must always be treated quantum mechanically due to their low mass. Thus, deriving a single wavefunction that describes both the electron and nucleus is unfortunately as complicated as it sounds. This problem can be circumvented using the concept of separability as described in Ch. 14. It was shown that a multidimensional wavefunction can be expressed as the product of smaller parts: $\psi_{total} = \psi_1\psi_2$, which is possible so long as the Hamiltonian can be separated into terms that do not contain the same quantum operators. As it applies to the hydrogen atom, we can achieve separability by dividing the coupled motion of the proton and electron into relative and center of mass components. The center of mass is defined almost entirely by the proton, which means that the other component is for the electron. The total wavefunction can now be separated into two:

$$\psi_{total} \approx \psi_{electron} \cdot \psi_{proton}$$

Since the proton is $\sim 1800\times$ heavier than the electron we can assume that it isn't moving, which allows us to simply ignore its wavefunction. The consequence for taking this approach is that the factor of mass in the electron's Hamiltonian is replaced with the proton / electron reduced mass:

$$\mu = \frac{m_p m_e}{m_p + m_e} \sim m_e$$

Due to the fact that a proton is $\sim 1836\times$ heavier than the electron, the reduced mass is only 0.05% different from the electron mass.

Now that we have decided to focus solely on the electron with its reduced mass, we must define the Hamiltonian and then solve the wavefunction. To this end we will start with the kinetic energy operator. It must be three dimensional and use spherical coordinates since the hydrogen atom (and indeed all atoms) are round. As a result we expect it to be similar to that encountered for the 3D rigid rotor model from Chapter 14, although there is one correction. The radial component of the rigid rotor problem is a fixed quantity, making the radius (r) a parameter as opposed to an operator. This is not true for the hydrogen atom since the electron can approach (or move away) from the nucleus as much as it wants. As a result the correct form of the kinetic energy operator is:

$$\frac{-\hbar^2}{2\mu \cdot r^2} \cdot \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} sin(\theta) \frac{\partial}{\partial \theta} \right)$$

Here we will drop the accent mark on the $\hat{r}$, $\hat{\theta}$ and $\widehat{\phi}$ operators for clarity. Next we must tack on the Coulombic potential operator that describes the attraction between the nucleus and the electron:

$$\hat{V}(r) = \frac{e^2}{4\pi\varepsilon_0 r}$$

With the addition of the electrostatic component we apply the wavefunction to the Hamiltonian operator into the standard eigenvalue form $\hat{H}\psi(r,\theta,\phi) = E \cdot \psi(r,\theta,\phi)$ as:

\frac{-\hslash^2}{2\mu }\left(\frac{\partial }{\partial r}r^2\frac{\partial }{\partial r}+\frac{1}{r^2}\left\{\frac{1}{\sin^2\left(\theta \right)}\frac{{\partial }^2}{\partial {\phi }^2}+\frac{1}{\sin sinleft(\theta \right)\ }\frac{\p

Real nightmare fuel, isn't it? Like Australian snakes, or pretty much any animal down under.

15.2.1. Separability

As with every multivariable quantum mechanical Hamiltonian the first thing to do is to check for separability, here between r, θ and ϕ. This is important because we can't solve the wavefunctions otherwise. Right out of the gate we can see that there may be a problem due to a single term with all three variables: $\frac{1}{r^2}\frac{1}{sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}$. However, we can make progress towards separability by first multiplying everything by $\frac{-2\mu}{\hbar^2}r^2$:

\[\left(r^2\frac{\partial }{\partial r}r^2\frac{\partial }{\partial r}+\left\{\frac{1}{\sin^2\left(\theta \right)}\frac

ParseError: invalid DekiScript (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\right\}\right)\psi \left(r,\theta ,\phi \right)+\frac{2\mu }{\hslash^2}\frac{e^2}{4\pi {\varepsilon }_0r}r^2\psi \left(r,\theta ,\phi \right)=-\frac{2\mu }{\hslash^2}r^2\cdot E\cdot \psi (r,\theta ,\phi) \nonumber \]

The next step is to insert the separated solution: $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$ and divide out the same on the left as: $\frac{1}{R(r)Y(\theta,\phi)}\hat{H}R(r)\,Y(\theta,\phi)$:

\[\frac{r^2}{R\left(r\right)}\frac{\partial }{\partial r}r^2\frac{\partial }{\partial r}R\left(r\right)+\frac{2\mu }{\hslash^2}\frac{e^2}{4\pi {\varepsilon }_0r}r^2+\frac{1}{Y\left(\theta ,\phi \right)}\left\{\frac{1}

ParseError: EOF expected (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\right\}Y\left(\theta ,\phi \right)=-\frac{2\mu }{\hslash^2}r^2E \nonumber \]

Now we group all the r terms on one side and the angular θ and ϕ on the other:

\[\frac{r^2}{R\left(r\right)}\frac{\partial }{\partial r}r^2\frac{\partial }{\partial r}R\left(r\right)+\frac{2\mu }{\hslash^2}\frac{e^2}{4\pi {\varepsilon }_0r}r^2+\frac{2\mu }{\hslash^2}r^2E=\frac{1}{Y\left(\theta ,\phi \right)}\left\{\frac{1}

ParseError: EOF expected (click for details)

sinleft(\theta \right)frac{\partial }{\partial \theta }\right\}Y\left(\theta ,\phi \right) \nonumber \]

We assume that the angular wavefunction $Y(\theta,\phi)$ is the same as encountered for the 3D rigid rotor, i.e. the spherical harmonics $Y_{l,m}$ discussed in Chapter 14, section 14.2.3. Based on the information derived from the 3D rigid rotor problem the right (angular) side of the expression $\frac{1}{Y_{l,m}}\hat{H}(\theta,\phi)\,Y_{l,m}$ is equal to $l(l+1)$, where the l quantum number is $l = 0,\ 1,\ 2$, etc. This leaves the radial part to solve as:

$$\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2 + \frac{2\mu}{\hbar^2}r^2E = l(l+1)$$

After some algebra and rearrangement we find:

$$\frac{-\hbar^2}{2\mu}\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) - \frac{e^2}{4\pi\varepsilon_0 r}r^2 + \frac{\hbar^2}{2\mu}l(l+1) = r^2E$$

To return the above into an eigenvalue form we simply multiply by $\frac{R(r)}{r^2}$ to reveal the radial Schrödinger equation:

$$\frac{-\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right)R(r) - \frac{e^2}{4\pi\varepsilon_0 r}R(r) = E \cdot R(r)$$

This differential equation has to specify a value of the angular momentum quantum number l before solving it, which means that there will be an l dependence to the solutions as shown below. With the wavefunctions in hand the energy of the hydrogen atom can be determined:

$$E=-\frac{\mu\cdot e^{4}}{32\pi^{2}\varepsilon_{0}^{2}\hbar^{2}}\frac{1}{n^{2}}$$

which is found to depend on a “principal” quantum number n = 1, 2, 3 etc. This quantum mechanical equation for energy is identical to that predicted by the Bohr model and conforms to the Balmer and Rydberg equation for spectroscopic transitions. The energies are negative due to the Coulomb potential as shown in Figure 15.2. As in all our previous examples the quantization occurs from a boundary condition, which for the hydrogen atom is that $R(r)\rightarrow 0$ as $r\rightarrow\infty$. Examination of the wavefunctions as discussed below reveal that n is related to the size of the orbital which we will now refer to as a “shell”. Degeneracies may be observed because, for any given principal quantum number n, there are $l=0,\ 1,\ 2\ldots(n-1)$ solutions to the radial equation. In fact there are even more degeneracies due to the angular part of the Hamiltonian, as for each l there are $2l$ +1 more states as defined by the $m_l=-l\ldots 0\ldots l$ quantum number. Hence, it must be true that the first shell state (n = 1) has no angular momentum ($l=0$) and is nondegenerate. In contrast, the n = 2 state has four degenerate wavefunctions characterized by $l=0$ (2s orbitals) and $l=1$ (2p orbitals). The 2p state has three wav efunctions that we know as p_x, p_y and p_z. The third and fourth shell can have l = 2 (d orbitals, describing transition metals) and l = 3 (f orbitals, characteristic of the actinides and lanthanides).

15.2.1. Quantum numbers and the periodic table

The dependencies of the various quantum numbers for the hydrogen atom are what give the periodic table its overall shape. Shown in Figure 15.3 is a representation based solely on quantum numbers; the rows are arranged according to the shell, which is the same thing as the principal quantum number n. The columns are arranged by the l quantum number, and each l block is $2l+1$ wide due to the m_l states. However, the overall arrangement of elements in Figure 15.3 is very different than the periodic table as you know it, which is arranged with the l blocks starting from s, f (tucked underneath) d, and finally p. This arrangement is due to the phenomenon of shielding that causes electrons to fill into orbitals according to that arrangement rather than monotonically with l as the atomic number Z increases. Shielding is discussed further below.

15.3: Hydrogen Radial Wavefunctions

Before we study the wavefunctions, we will first make some approximations to the Hamiltonian that simulate the electron's behavior at short and long distances. For example, what does the radial Schrödinger equation say about the electron if it is highly displaced from the nucleus (at large r)? First, we can use the product rule to show that the kinetic energy operator $\frac{1}{r}\frac{\partial^2}{\partial r^2}r$ is equivalent to $\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$ (you might demonstrate this as a homework assignment). We make this substitution in the kinetic energy operator because, when the Hamiltonian is multiplied by r:

$$\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}-\frac{l\,(l+1)}{r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right)r\cdot R\,(r)=E\cdot r\cdot R\,(r)$$

This shows us that, if $r\to\infty$ we can remove the potential energy terms: $\frac{l(l+1)}{r^2}-\frac{e^2}{4\pi\varepsilon_0 r}$ leaving:

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}r\cdot R\,(r)=E\cdot r\cdot R\,(r)$$

At long distances we can also make the approximation: $\frac{\partial^2}{\partial r^2}r\cdot R\,(r)\to r\frac{\partial^2 R(r)}{\partial r^2}$. Next we simply divide by r to find:

$$\frac{\partial^2}{\partial r^2}R\,(r)=\frac{-2\mu}{\hbar^2}E\cdot R\,(r)$$

The solution is $R\,(r)=e^{-c\cdot r}$, where $c=\sqrt{\frac{-2\mu E}{\hbar^2}}$ and has units of inverse length. It may appear that $\sqrt{\frac{-2\mu E}{\hbar^2}}$ should be imaginary; however, this isn't the case because the energies of the hydrogen atom are negative. What is important is that the wavefunction exponentially decays at large distance, which means that the electron very much wants to remain in proximity to the nucleus.

At short distances $(r\to 0)$ we remove the $\sim r^{-1}$ Coulombic potential energy while retaining the angular momentum term $\frac{-\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$ due to its $\sim r^{-2}$ dependence. Likewise we also make the approximation $E\cdot r\cdot R\,(r)\to 0$ to yield:

$$\frac{\partial^2}{\partial r^2}r\cdot R\,(r)-\frac{l\,(l+1)}{r}R\,(r)=0$$

A solution is $R\,(r)=r^l$ as verified below:

$$\frac{\partial^2}{\partial r^2}r\cdot r^l-\frac{l\,(l+1)}{r}r^l=\frac{\partial^2}{\partial r^2}r^{l+1}-l\,(l+1)\,r^{l-1}=l\,(l+1)\,r^{l-1}-l\,(l+1)\,r^{l-1}=0$$

What this means is that the radial wavefunctions have different behavior as a function of angular momentum. This is due to the increase in rotational kinetic energy as the electron approaches the nucleus. In fact it would gain infinite kinetic energy at $r=0$, although at small distances the fact that $R\,(r)\approx r^l\to 0$ prevents this from happening.

The analysis above demonstrates that the radial wavefunctions must have short and long-distance components, with a mathematical entity that bridges the two:

$$R\,(r)\approx r^l\cdot(?)\cdot e^{-r}$$

This behavior is borne out from the "generalized Laguerre polynomials"; these are solutions to a related differential equation that were derived in 1880. In fact, it is the Laguerre polynomials that are responsible for the quantization of energy because, if the principal quantum number n wasn't an integer, then the wavefunctions wouldn't go to 0 at large distances. The complete radial wavefunctions are listed in Table 15.1.

15.3.1 Properties of the radial wavefunctions

The hydrogen atom's radial Schrödinger equation "controls" the energy via the principal quantum number n. As a result we can examine various features of the radial wavefunctions as they reveal the inner energetic workings of the simplest atom. This information can then be used to build up our knowledge of more complex (multielectron) atoms and eventually molecules. The most sensible organization scheme on hydrogen's electronic properties is based on the shell and angular momentum as characterized by the n and l quantum numbers; in fact the radial wavefunctions are labeled as $R_{n,l}(r)$.

15.3.1.1 The $l = 0$ states

Atomic states with no angular momentum are of the “s” type, and the radial wavefunctions for the first three s-state shells are shown in Figure 15.4 A, B. The 1s wavefunction $R_{1,0}(r) = N \cdot e^{\frac{-r}{a_0}}$ is a simple exponential decay from the origin. The 2s and 3s states are similar, although they have an increasing number of nodes that raises the energy and maintains orthogonality between different eigenstates. The most important feature of the s-states wavefunctions is that they are finite at the origin (i.e. $R_{n,l=0} > 0$ at $r = 0$). The reason that this is allowed is because there is no rotational kinetic energy: $\frac{\hbar^2}{2\mu \cdot r^2} l(l+1) = 0$ that would erstwhile become infinitely high as $r \to 0$. Most interesting is the fact that the s-states are ostensibly degenerate with their higher angular momentum siblings within the same shell; however, as discussed later the phenomenon of shielding energetically favors the s-states.

15.3.1.2 Radial distribution functions

According to Coulomb’s Law if the electron “touches” the nucleus then an infinite amount of energy will be released that would destroy the Universe. The fact that the s-state wavefunctions are finite at $r = 0$ suggests this possibly; however, universal annihilation is thwarted because electron never “finds” the nucleus since it is a point particle. In more technical language, the probability that the electron resides exactly within the same volume as the nucleus is 0%. This fact reveals that it is desirable to represent this volume-probability relationship. To do so we simply multiply the volume-normalizing (Jacobian) $4\pi r^2$ factor times the absolute value of the radial wavefunctions $R^2_{n,l}$ as shown in Figure 15.4D. These are called radial distribution functions, and they provide a great way to communicate quantum information as one can now clearly see that the electron isn’t going to be found at the nucleus for any state. Furthermore, the radial separation between the various s-states due to the n-dependence of the wavefunctions $\sim e^{\frac{-r}{n \cdot a_0}}$ is more visible.

15.3.1.3 The $l > 0$ states

The fact that $R_{n,l>0} = 0$ at the origin is the most distinguishing feature of the higher angular momentum orbitals as seen in the 2p, 3p and 3d functions shown in Figure 15.4C. This is due to the $R(r) \approx r^l$ short length scale behavior originating from the rotational energy that is proportional to $\sim \frac{1}{r^2}$. This radial dependence means that, if the electron approaches the origin it will be spinning with near infinite energy; however, the suppression of wavefunction amplitude as $rto0$ prevents this. As seen in Figure 15.4C increasing the principal quantum number from the 2p to the 3p shell imparts a radial node that steps up the kinetic energy and maintains orthogonality. And while the 2p and 3p radial functions are clearly distinguished from each other, it is interesting to note that the 2p and 3d are similar in their overall shape due to a lack of nodes. The 4f state is similarly nodeless.

15.3.1.4 Degeneracies and magnetism

Due to the dependence of energy on the principal quantum number n one might ask, how do we even know that there are three p, five d and seven f m_l states? It’s because we can directly observe them, and to describe how we first note that an electron with angular momentum is a spinning charge. As such it creates its own magnetic field, the direction of which is proportional to $-m_l$ (the minus sign is a result of the negative charge of the electron). This is why m_l is often called the “magnetic quantum number”. Let’s analyze the 2p $(l = 1)$ state’s three $m_l = -1,\ 0,\ 1$ sub-states. Since the $m_l = 1$ and $m_l = -1$ have opposing magnetic fields, an external field will interact to split their energies while the $m_l = 0$ state isn’t affected. As a result the m_l degeneracies are lifted which can be observed using fluorescence spectroscopy. Pieter Zeeman first did so in 1896 using sodium and lithium. The so-called Zeeman effect allowed Hendrik Lorentz to predict the properties electrons before the electron was even discovered, and as a result Lorentz and Zeeman won the Nobel Prize in 1902. Later m_l state splitting was observed due to the application of a strong electric field on hydrogen by Johannes Stark in 1913. This effect could only be accurately described using quantum theory which was considered one of the early validations of quantum mechanics, and Stark was awarded the Nobel Prize in 1919.

15.4: Spin-Orbit Coupling

A curious thing about the hydrogen atom is that the 2p states always appear split *even if no magnetic field has been applied!* This phenomenon originates from the fact that and any electron in a $l > 0$ state has orbital rotation that creates a magnetic field, just as discussed in the previous section. This field then acts upon the intrinsic magnetism of an electron, which exists due to its spin angular momentum. Essentially, they are like little bar magnets. Thus, the orbital and spin magnetic fields can either be aligned (higher energy) or not (lower energy). This effect is called spin-orbit coupling and is depicted in Figure 15.5.

The Hamiltonian for this interaction can be derived from the Einstein's theory of relativity:

$$\hat{H}_{SO} = -\frac{\mu_B}{\hbar m_e e c^2}\frac{1}{r}\frac{\partial \hat{V}}{\partial r}\hat{L}\cdot\hat{S}$$

where $\mu_B = 9.274\ J\cdot T^{-1}$ is the Bohr magneton that describes the magnetic moment of an electron due to orbital or spin angular momentum. The constants and gradient of the potential are generally lumped into a constant "A" such that $\hat{H}_{SO} \sim A\cdot\hat{L}\cdot\hat{S}$. The dot product of the two operators is defined as any standard vector: $\hat{L}\cdot\hat{S} = \hat{l}_x\cdot\hat{s}_x + \hat{l}_y\cdot\hat{s}_y + \hat{l}_z\cdot\hat{s}_z$. However, we cannot use this expression because the uncertainty principle dictates that we cannot know the x, y, and z components of angular momentum simultaneously. As a result, we employ an alternative strategy where we calculate the total angular momentum using the $\hat{J}$ operator, where $\hat{J} = \hat{L} + \hat{S}$. We encountered the issue of addition of angular momentum in Ch. 14, so you might want to review that section. Regardless, the operator $\hat{J}^2$ contains the $\hat{L}\cdot\hat{S}$ dot product:

$$\hat{J}^2 = \left(\hat{L}+\hat{S}\right)^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L}\cdot\hat{S}$$

We can rearrange the above to show that: $\hat{L}\cdot\hat{S} = \frac{1}{2}\left\{\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right\}$, where the $\hat{J}$, $\hat{L}$, and $\hat{S}$ operators return their respective quantum numbers (j, l and s) such that the interaction is:

$$E_{SO} = \frac{A}{2}\cdot\{j(j+1) - l(l+1) - s(s+1)\}$$

This spin-orbit energy is a unique function of the electronic configuration of an atom or molecule. To understand exactly how this works we will provide an example for a hydrogen atom with a 2p^1 electron configuration, i.e. $l = 1$ and $s = \frac{1}{2}$. As discussed in Ch. 14 the l and s angular momenta add to produce two possible j states:

$$j = |l+s| = \frac{3}{2}\ or\ j = |l-s| = \frac{1}{2}$$

Term symbols ($^{2S+1}\mathrm{L}_j$) distinguish between the two as having $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ electronic configurations. Spin-orbit coupling raises the energy of the $^2P_{\frac{3}{2}}$ state:

$$E_{SO} = A\cdot\left\{\frac{3}{2}\left(\frac{3}{2}+1\right) - 1(1+1) + \frac{1}{2}\left(\frac{1}{2}+1\right)\right\} = \frac{A}{2}\cdot\left\{\frac{15}{4} - \frac{8}{4} - \frac{3}{4}\right\} = \frac{A}{2}$$

while the $^2P_{\frac{1}{2}}$ state is pushed downhill:

$$E_{SO} = A\cdot\left\{\frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right\} = \frac{A}{2}\cdot\left\{\frac{3}{4} - \frac{8}{4} - \frac{3}{4}\right\} = -A$$

Consequently the otherwise degenerate $^2P_{\frac{3}{2}}$ and $^2P_{\frac{1}{2}}$ configurations are split as shown in Figure 15.6. Also shown is how the spin-orbit effect is observed from the H$_\alpha$ fluorescence which is the target of astronomers for charting the galaxy.

Hydrogen's spin-orbit coupling is very small and can only be observed with a fine spectrometer. However, the spin-orbit Hamiltonian's A constant is a function of the gradient of the Coulombic potential energy: $\frac{\partial\hat{V}}{\partial r}$, which in turn is proportional to the atomic number (Z) of an element as Z^4. This has two effects; one is that the spin-orbit energy becomes overwhelmingly strong for high Z elements. Second, the spin-orbit effect means that the total wavefunction cannot have the orbital and spin wavefunctions separated as: $\psi_{total} \neq \psi_{space}\cdot\psi_{spin}$. This introduces significant problems when trying to classify these atoms using term symbols and order their energy levels. Unfortunately this is very difficult to deal with, and the development of theoretical calculations that incorporate spin-orbit effects is a topic of current research.

15.5: Spectroscopy

Spectroscopy is the most common method of characterizing chemical and biological compounds. While the absorption of light can be attributed to dynamics such as electronic (visible), vibrational (infrared), or rotational (microwave) excitation, one must apply quantum mechanics connect a spectrum to molecular physical properties. We are especially concerned with what makes an atom or molecule absorb light at all! As shown here, such information necessitates knowledge of the ground and excited state wavefunctions of a molecule's Hamiltonian as solved by the Schrödinger equation.

One of the central tenets of quantum mechanics is that all observables have associated operators. Absorption of light is (mostly) due to the interaction of the photon's electric field with the dipole moment of an atom or molecule. To absorb light there must be a change in the dipole moment, which is defined from classical electromechanics as $\overrightarrow{\mu} = q_1 q_2 \overrightarrow{r}$. Here, q_1 and q_2 are the charges (for hydrogen, and electron and proton) and $\overrightarrow{r}$ is the distance between. The quantum mechanical analog is the dipole operator, which for the hydrogen atom is:

$$\widehat{\mu} = -e^2 \cdot \hat{r}$$

We can calculate the expectation value of the dipole operator as it applied to a transition across energy states:

$$\langle\widehat{\mu}\rangle = -e \cdot \langle\psi_i\rangle = \int\int\int \psi_f^*(r,\theta,\phi) \cdot r \cdot \psi_i(r,\theta,\phi) \cdot \partial r \cdot sin(\theta)\,\partial\theta \cdot \partial\phi$$

This expression isn't quite the same as our previous examples of expectation values because different states are to the right and left of the operator. Here, ψ_i is the initial state of the atom or molecule; most likely this is the ground state. The "go-to" state is ψ_f, which must have a higher energy such that the difference in energy from the excited to the ground state matches the energy of the light absorbed:

$$\lambda = \frac{hc}{\Delta E}$$

The transition dipole moment $\langle\widehat{\mu}\rangle$, sometimes called the difference dipole moment, is related to the strength of the absorption. A large $\langle\widehat{\mu}\rangle$ means that the atom or molecule has a large Beer's Law (ε) constant, although it should be noted that the absolute strength of the transition dipole moment is not very quantitative. Mostly, $\langle\widehat{\mu}\rangle$ tells us whether absorption of light occurs or not. If $\langle\widehat{\mu}\rangle = 0$ then we say that the excited state is "optically silent". Otherwise, $\langle\widehat{\mu}\rangle > 0$ means that the transition between ground and excited states can occur through light absorption. We can also determine what molecular properties and dynamics allow for a non-zero $\langle\widehat{\mu}\rangle$; these are called selection rules.

The fact that light is polarized is an important detail when calculating the transition dipole moment. As shown in Figure 15.7, the oscillation of the photon's electric field must be represented in the dipole operator. To demonstrate we study the case of x-polarized light impinging on the 1s ground state of a hydrogen atom. To describe this correctly the dipole operator must align in the x direction, requiring a modification of the dipole operator as:

$$\widehat{\mu} = -e^2 \cdot \hat{x}$$

Since atoms are round and we are working in spherical coordinates, we have to substitute the x coordinate in the spherical form as: $\widehat{\mu} = -e^2 \cdot r \cdot sin(\theta)cos(\phi)$. Inserting this into the expression for calculating difference dipole moment yields:

$$\langle\widehat{\mu}\rangle = \int_0^\infty \psi_f^*(r) \cdot r \cdot \psi_i(r) \cdot 4\pi r^2 \partial r \cdot \int_0^\pi \psi_f^*(\theta)\,\psi_i(\theta) \cdot sin^2(\theta) \cdot \partial\theta \cdot \int_0^{2\pi} \psi_f^*(\phi)\,\psi_i(\phi) \cdot cos(\phi) \cdot \partial\phi$$

An interesting fact of this expression is that, while we think of the radial component as being overwhelmingly important, here it isn't so. The radial integral is non-zero for any combination of initial and final states, yet, we know from experiment that hydrogen is selective as to what transitions are optically allowed. In fact, the difference dipole moment is dependent on the angular integrals, as $\langle\widehat{\mu}\rangle \neq 0$ *if and only if the change in angular momentum quantum number from the ground to excited state is* $\Delta l = \pm 1$. This spectroscopic selection rule is consistent with the fact that a photon has an angular momentum of $l = 1$, which conserves angular momentum upon absorption of light. Thus, the ground 1s state of hydrogen can only transition to a 2p state (x, y or z) depending on the polarization of light. Likewise if a hydrogen atom is in an excited 2p state it can transition only to the 3s or one of the 3d states. There are also selection rules about Δm_l depending on the light polarization and the initial and final states. Last, the process of fluorescence is analogous to absorption in reverse, where a drop from an excited state to the ground state creates a photon. The same $\Delta l = \pm 1$ selection rule applies.

15.6: Multielectron Atoms and Exchange

Having exhausted our investigations into hydrogen, we now study helium as the next element on the periodic table. This atom has two electrons to balance out the nuclear charge of Z = +2. Due to the extra electron we now must solve a larger Schrödinger equation with a Hamiltonian that more than doubles in size:

$$\hat{H}(1,2)=\frac{-\hbar^2}{2\mu r^2}\nabla_1+\frac{-\hbar^2}{2\mu r^2}\nabla_2-\frac{e^2}{4\pi\varepsilon_0 r_1}-\frac{e^2}{4\pi\varepsilon_0 r_2}+\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}$$

where ∇ is called the "Laplacian" operator that returns all the kinetic energy including rotational. The reason that the Hamiltonian more than doubles is because there is an electron-electron repulsive (energy raising) term: $\frac{+e^2}{4\pi\varepsilon_0|r_1-r_2|}$, which unfortunately creates a problem for solving the wavefunctions. To explain, note that without this part the Hamiltonian can be separated into terms for either electron 1 or 2 only. Thus, the total wavefunction is separable into the product of two individual states:

$$\psi_{total}(1,2)=\psi_1(1)\psi_2(2)$$

where the "[GrindEQ__1_]" and "[GrindEQ__2_]" are labels for the first and second electron and the subscripts on ψ_1 and ψ_2 refers to what type of orbital (1s, $2p_x$ etc.) that the electron resides. We expect that the individual electron states are the same as the hydrogen atom albeit with a higher nuclear charge of Z=+2. The He wavefunction for the ground state $1s^2$ configuration should be {\psi }_{1S}\\label{1_}{\psi }_{1S}\\label{2_}.

However, none of this is true because the $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ term completely negates the ability to separate the Hamiltonian into "mini" Schrödinger equations for electrons 1 and 2. Maybe you are expecting us to introduce a clever math trick that allows us to derive the real wavefunctions- actually there isn't one. *We don't know what the real wavefunctions are for any atom or molecule with more than one electron.*

Even though the separation solution {\psi }_{total}(1,2)\approx {\psi }_1\\label{1_}{\psi }_2\\label{2_} isn't correct, we use it anyways due to the fact that we are confronted with a problem with no simple solution. This approximation requires us to employ a variety of different approaches for developing a quantum-based understanding of multielectron atoms. For example, since a separated solution is not an eigenstate of the multielectron Hamiltonian:

$$\hat{H}\psi_1(1)\psi_2(2)\neq E\cdot\psi_1(1)\psi_2(2)$$

we cannot use the eigenvalue way of solving the energy. However, we can employ the expectation value approach: $\langle E\rangle=\int\psi^*\hat{H}\psi$. While it is comforting that we have some mathematical tools at our disposal, the expectation value nonetheless is not real energy of the atom because the separated wavefunctions allow the two electrons to partially overlap each other in the same space at the same time. This energy raising mistake is called the "correlation error", and it causes $\langle E\rangle$ to be higher than the real energy. Methods to mitigate the correlation error can be complex and are usually introduced in graduate-level courses in quantum mechanics.

15.6.1 The Variational Principle. The use of an approximate ψ solution to the multielectron Hamiltonian causes the $\langle E\rangle$ expectation value to always be greater than the true energy:

$$\int\psi^*\hat{H}\psi>E_{exact}$$

This provides an interesting approach to create better wavefunctions for multielectron atoms and molecules using what is called the Variational Principle. What we do is alter and adjust our "best guess" separated wavefunctions to achieve the lowest $\langle E\rangle$ possible, as any change that results in a lower energy is better. Here is an example; if we are trying to optimize a quantum mechanical description for the helium atom ground state using a separated solution: {\psi }_{total}(1,2)\approx {\psi }_{1S}\\label{1_}{\psi }_{1S}\\label{2_}, we first re-derive the hydrogen ψ_{1S} using the variable Z for the atomic number. These are called "hydrogen-like" wavefunctions, which for the 1s state is:

$$\psi_{1,0}(r,Z)=2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}e^{\frac{-Z\cdot r}{a_0}}$$

(recall that Z = +1 for hydrogen). Next, we insert this function for electrons 1 and 2 and apply it to calculate the $\langle E\rangle$ expectation value for the helium atom. The result is a function of Z, which we then adjust to achieve the lowest energy possible. To do so we find the best $\langle E\rangle$ by applying standard calculus definition of the minimum of a function:

$$\frac{\partial}{\partial Z}\int\psi_{1S}(1)^*\psi_{1S}(2)^*\hat{H}\psi_{1S}(1)\psi_{1S}(2)=0 \text{ @ } Z_{opt}$$

While Z = +2 for helium, applying the above method we find that Z_{opt}= +1.7. While the lower atomic charge may seem arbitrary, in fact one can understand why such alterations make sense based on physical grounds. In this example, reducing the effect of the nuclear charge in the helium atom wavefunction means that the electrons screen each other from the nucleus. This has a substantial effect on atomic energies as discussed below. And while changing the apparent nuclear charge improves our description of the multielectron wavefunction, it's not a perfect solution and further optimizations are necessary. In fact, this is one of the most active areas of research in chemical theory.

15.6.2 Shielding. An electron's attraction to the nucleus is offset by repulsive interactions with other electrons. This is easy to imagine for electrons in different shells because one electron is closer to the nucleus than the other. As a result, one can say that the higher shell electron is "shielded" from the positive nuclear charge. The shielding effect also operates within the l states (s, p, d etc.) of the same n shell, which results in a loss of their degeneracy. The reason for this can be seen in the 2s and 2p wavefunctions in Figure 15.4, where the 2s has amplitude near r = 0 while the 2p doesn't. As a result, in a multielectron atom the 2s electron's energy is lowered at the expense of the 2p.

This trend continues across states of increasing angular momentum, and as a result the 3s state is lower in energy than the 3p, which in turn is lower in energy than the 3d. In fact, the effect of shielding is so substantial the 4s state is lower in energy than the 3d! Let's use radial wavefunctions to demonstrate. At first, the reordering of 4s < 3d appears incorrect because the average electron-nuclear distance of a hydrogenic 4s state is $\langle r\rangle_{4s}=\int_0^\infty R_{4s}^*\cdot r\cdot R_{4s}(r)\cdot r^2\partial r=24\cdot a_0$, which is much longer than $\langle r\rangle_{3d}=10.5\cdot a_0$ of a 3d electron. The 4s electron's greater $\langle r\rangle$ implies that it is higher in energy than the 3d. However, the shielding effect occurs close to the nucleus. Thus we must alter our approach by calculating $|R_{4s}(r)|^2$ and $|R_{3d}(r)|^2$over the shorter distance range of 0 → a_0. Integral of the absolute value of the 4s wavefunction yields: $\int_0^{a_0}R_{4s}^*\cdot R_{4s}(r)\cdot r^2\partial r=$

\[\frac{1}

ParseError: EOF expected (click for details)

^2\cdot r^2\partial r=4.1\times {10}^{-3} \nonumber \]

When we perform the same calculation using the 3d radial wavefunction we find:

\[\int^{a_0}_0{}

ParseError: invalid DekiScript (click for details)

^*\cdot {\mathit{\Psi}}_{3d}\cdot r^2\partial r=6.5\times {10}^{-6} \nonumber \]

As a result, the 4s electron is more likely to be within 0 →a_0 of the nucleus by a factor of ∼630× compared to the 3d. In turn the 4s electron soaks up more Coulombic energy by ∼1000×, which is why a multielectron atom has a lower energy 4s orbital compared to 3d. Don't forget, however, that 4s is higher in energy that the 3d in a 1-electron hydrogenic atom as shielding only occurs if there are multiple electrons.

When applied across all elements shielding reorders the periodic table into its familiar form shown in Figure 15.8. A diagram to remember the state ordering is also presented. We conclude this section with one last effect on atomic structure due to the effects of relativity. For very heavy elements such as gold (Z=79), the 1s electrons experience an extremely high positive nuclear charge that considerably increases the electrons' kinetic energy. Thus, the velocities approach that of light, which causes an increase in mass and a contraction of the 1s orbital's radius. This is consistent with the fact that the Bohr unit of length is inversely proportional to mass. This relativistic effect causes gold and other heavy elements of the 6^{th} and 7^{th} row to reverse erstwhile normal trends of the periodic table concerning electron binding energies and oxidation states. The relativistic effect has also been used to explain why the periodic table appears to come to an end. If the atomic number Z becomes too high then 1s electrons simply become too unstable such that the element can't exist.

15.6.3 The Pauli exclusion principle and Slater determinants. In Ch. 14 it was discussed how spin is an angular momentum-like property of an electron. The spin wavefunctions are $\psi_{spin} = \alpha$ (the "up" ↑ state) and $\psi_{spin} = \beta$ (the "down" ↓ state). The $\hat{S}_z$ operator acts upon them as:

$$\hat{S}_z\alpha = s_z \cdot \alpha = ½\hbar \cdot \alpha \; and \; \hat{S}_z \cdot \beta = s_z \cdot \beta = -½\hbar \cdot \beta$$

Likewise $\hat{S}\alpha = \sqrt{s\,(s+1)}\,\hbar \cdot \alpha$ and $\hat{S}\beta = \sqrt{s\,(s+1)}\,\hbar \cdot \beta$. Last, we note that the spin states are orthonormal:

$$\int \alpha^*\alpha = \int \beta^*\beta = 1 and int \alpha^*\beta = \int \beta^*\alpha = 0$$

Electrons are assigned spin wavefunctions by labeling them as such; for example, $\psi_{spin} = \alpha\,(1)\,\beta\,(2)$ for an orbital with an up and down electron (↑↓).

One "rule" of the Universe is that particles with ½$\hbar$ spin angular momentum cannot occupy the same quantum state at the same time. This is called the Pauli exclusion principle, and it is the reason why you can't have an atomic orbital hold two electrons of the same spin: ↑↑ $= \alpha\,(1)\,\alpha\,(2)$. Rather they must have opposite s_z as: ↑↓ $= \alpha\,(1)\,\beta\,(2)$. To include spin into our multielectron wavefunction we simply express it as the product of space and spin. Consequently, it would appear that the multielectron wavefunction for helium's $1s^2$ ↑↓ configuration is:

$$\psi\,(1,2) = \psi_{space}\,(1,2)\,\psi_{spin}\,(1,2) = \psi_{1S}(1)\alpha\,(1) \cdot \psi_{1S}(2)\beta\,(2)$$

However, this approach easily allows us to create a wavefunction for a $1s^2$ ↑↑ configuration that violates the Pauli principle: {\psi }_{1S}\\label{1_}\alpha \left(1\right)\cdot {\psi }_{1S}\\label{2_}\alpha \left(2\right). This cannot be correct, which causes us to enforce the Pauli principle by imparting a mathematical property called "inversion to interchange" defined by:

$$\psi\,(1,2) = -\psi\,(2,1)$$

This means that, upon exchanging the labels on an electron pair, the wavefunction should become the opposite of its former self. Any multielectron wavefunction that has this property satisfies the Pauli exclusion principle as shown below.

15.6.3.1 Singlet States. A singlet state is one with an even number of electrons that are equally split between up and down spins. This is called a "low spin" configuration and is diamagnetic; most chemical compounds have low spin electronic ground states. We will demonstrate the effects of the Pauli exclusion principle by developing an appropriate singlet $1s^2$ ↑↓ ground state helium wavefunction. While it appears that the inversion to interchange property: $\psi\,(1,2) = -\psi\,(2,1)$ might be mathematically intractable, in fact this is trivial to engineer. Beginning with the total wavefunction divided into space and spin components as:

$$\psi_{total}\,(1,2) = \psi_{space}\,(1,2) \cdot \psi_{spin}\,(1,2)$$

We create the inversion to interchange property within the spin manifold as:

$$\psi_{spin}\,(1,2) = \alpha\,(1)\,\beta\,(2) - \alpha\,(2)\,\beta\,(1)$$

To verify, we exchange the electron's labels to find:

\alpha \left(2\right)\beta \left(1\right)-\alpha \left(1\right)\beta \left(2\right)=-left\{\alpha \left(1\right)\beta \left(2\right)-\alpha \left(2\right)\beta \left(1\right)\right\} \nonumber

This is antisymmetry property we are looking for. The total singlet ground state wavefunction with space and spin is therefore:

$$1\,\mathit{\Psi}(1,2) = \psi_{space}\psi_{spin} \approx \psi_1(1)\psi_2(2)\left\{\frac{\alpha\,(1)\,\beta\,(2) - \alpha\,(2)\,\beta\,(1)}{\sqrt{2}}\right\}$$

where the $\frac{1}{\sqrt{2}}$ is a normalization factor. It is now evident how the creation of an "illegal" $1s^2$ \(\uparrow \uparrow)configuration for helium is avoided:

$$\psi_1(1)\psi_2(2)\left\{\frac{\alpha\,(1)\,\alpha\,(2) - \alpha\,(2)\,\alpha\,(1)}{\sqrt{2}}\right\} = 0$$

due cancellation of the spin wavefunctions. There is one more property that is required, which is that it shouldn't be possible to distinguish between the two electrons. This is accomplished by altering the real space orbital manifold as:

\[1\mathit{\Psi}\left(1,2\right)=\left\{\frac

ParseError: invalid DekiScript (click for details)

\right\}\left\{\frac{\alpha \left(1\right)\beta \left(2\right)-\alpha \left(2\right)\beta \left(1\right)}{\sqrt{2}}\right\} \nonumber \]

This works because electron 1 can be in either the first or second spatial orbital, and the same is true for the 2^{nd} electron. As a result they are not identifiably different.

15.6.3.2 Triplet states. A high spin electronic configuration has an unbalanced number of up and down electrons. The triplet is the most common example and occurs when the number of spin up and down electrons differ by 2. In Chapter 14 we discussed how spin angular momenta add to create three possible triplet spin wavefunctions:

$$\psi_{spin} = \alpha\,(1)\,\alpha\,(2)\;\; psi_{spin} = \beta\,(1)\,\beta\,(2)\,\psi_{spin} = \frac{1}{\sqrt{2}}\{\alpha\,(1)\,\beta\,(2) + \alpha\,(2)\,\beta\,(1)\}$$

The above are symmetric with respect to interchange of the electron's labels, we must impart antisymmetry to the spatial wavefunctions as follows:

\[3\mathit{\Psi}\left(1,2\right)=\left\{\frac

ParseError: invalid DekiScript (click for details)

\right\}\left\{\alpha \left(1\right)\alpha \left(2\right)beta \left(1\right)\beta \left(2\right)frac{1}{\sqrt{2}}\left\{\alpha \left(1\right)\beta \left(2\right)+\alpha \left(2\right)\beta \left(1\right)\right\}right\} \nonumber \]

It is very uncommon to observe molecules with triplet ground states as the Pauli principle forbids two up or down spins from occupying the same space orbital. However, it is more frequently observed in excited electronic states, especially as a high spin configuration can be lower in energy compared to an equivalent singlet state as discussed below. An exception is molecular oxygen that is a ground state triplet. This fact dictates much about O_2's reactivity with organics, which has important implications for oxidation of biological molecules and materials.

15.6.3.3 Slater Determinants. While the ability to write antisymmetrized wavefunctions for two electrons isn't particularly difficult, one runs into greater complexity when trying to do the same for more electron rich systems. For example, in the case of a three electron atom, the principle of antisymmetry requires the permutation of any pair of electrons result in a negative wavefunction:

$$\psi\,(1,2,3) = -\psi\,(2,1,3) = -\psi\,(1,3,2) = -\psi\,(3,2,1)$$

It isn't clear how to mathematically engineer these relationships into a single wavefunction. In 1929 John Slater developed a method to do so using matrices, where the orbital identity change down the column while the electron identity moves to the right across the row. The wavefunction is the normalized determinant of this configuration. Let's practice by creating a helium two electron $1s^1\ 2s^1$ triplet state the wavefunction:

`3\mathit{\Psi}=det\frac{1}{\sqrt{2}}\left|{\mathit{\Psi}}_{1s}\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_{1s}\left(2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_{2s}\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_{`

Expanding the determinant reveals:

$$3\,\mathit{\Psi}=\frac{1}{\sqrt{2}}\{\,\mathit{\Psi}_{1s}\,(1)\,\alpha\,(1)\ \mathit{\Psi}_{2s}\,(2)\,\alpha\,(2)-\ \mathit{\Psi}_{2s}\,(1)\,\alpha\,(1)\ \mathit{\Psi}_{1s}\,(2)\,\alpha\,(2)\}$$

This expression is equal to: $\frac{1}{\sqrt{2}}\{\psi_{1s}\,(1)\,\psi_{2s}\,(2)-\psi_{2s}\,(1)\,\psi_{1s}\,(2)\}\,\alpha\,(1)\,\alpha\,(2)$, exactly as we determined previously. The singlet $1s^2$ ↑↓ ground state configuration of helium requires two determinants:

`1\mathit{\Psi}=det\frac{1}{2}\left(\left|{\mathit{\Psi}}_{1s}\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_{1s}\left(2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_{1s}\left(1\right)\beta \left(1\right)\ {\mathit{\Psi}}_{1s}`

Simplification yields:

$$\frac{1}{2}\{\,\mathit{\Psi}_{1s}\,(1)\ \mathit{\Psi}_{1s}\,(2)+\ \mathit{\Psi}_{1s}\,(1)\ \mathit{\Psi}_{1s}\,(2)\}\ \{\alpha\,(1)\,\beta\,(2)-\alpha\,(2)\,\beta\,(1)\}$$

which is identical to the expression derived earlier.

Next on the periodic table is lithium, which has a $1s^2\ 2s^1$ configuration for its three electrons. The wavefunction in the determinant form is:

`\mathit{\Psi}=det\frac{1}{\sqrt{3}}\left|{\mathit{\Psi}}_{1s}\left(r_1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_{1s}\left(r_2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_{1s}\left(r_3\right)\alpha \left(3\right)\ {\mathit{\Psi`

We won't expand the determinant here; however, if we did so and switched any two electron labels, we would find that the resulting total wavefunction has picked up a "-" sign as required by the Pauli principle. The addition of more electrons creates an even more complex state, which is why one needs supercomputers to model large molecules such as proteins using quantum mechanics.

15.6.4 Exchange energy and magnetism. The effects of Pauli principle are substantial due to the antisymmetry of wavefunctions. This in turn affects energetic ordering of excites states as a function of spin. To demonstrate we will study the dynamics of excitation of the helium atom shown in Figure 15.9A. The singlet $1s^2$ ground state transitions into the singlet $1s^1\ 2p_z{}^1$ excited state of helium after absorption of z-polarized light due to the angular momentum selection rule. While a spin selection rule stipulates $\langle\hat{\mu}\rangle=0$ for excitation to the triplet state, the excited singlet may intersystem cross into a high spin $1s^1\ 2p_z{}^1$ configuration nonetheless. As a result we will study the difference in the singlet and triplet state energies by applying the antisymmetrized wavefunction to the electron-electron Coulomb operator:

\[\int{}

ParseError: invalid DekiScript (click for details)

^1\left(1,2\right)\cdot \partial \tau int{}

ParseError: invalid DekiScript (click for details)

^3\left(1,2\right)\cdot \partial \tau \ \nonumber \]

These integrals are evaluated in full in the Appendix, where we demonstrate that the many terms collapse into the form K + J, where the term K is the Coulomb integral:

$$K=\int\psi_1^*(1)\psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0\,|r_1-r_2|}\psi_1(1)\psi_2(2)\cdot\partial\tau=\int|\psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0\,|r_1-r_2|}|\psi_2(2)|^2\cdot\partial\tau$$

This describes the probability density of the first electron in the first orbital, `{\left|{\psi }_1\\label{1_}\right|}^2`, electrostatically interacting with the same for the second electron `{\left|{\psi }_2\\label{2_}\right|}^2`. This is essentially identical to what was taught to you in Physics II Electromagnetism. Where this story gets more complex is that there is a second term found in the Coulombic interaction. It is called the exchange term and is usually abbreviated J:

$$J=\pm\int\psi_1^*(1)\psi_1(2)\frac{e^2}{4\pi\varepsilon_0\,|r_1-r_2|}\psi_2^*(2)\psi_2(1)\cdot\partial\tau$$

where + is for the singlet and – is for the triplet. Consequently, the excited triplet state of helium is slightly lower in energy as shown in Figure 15.9.

The exchange term describes electrons as being in two places at once. While this is hard to understand, the effect is very much real as the fact that the excited triplet state is lower in energy than the singlet has been verified experimentally. One reason for this is the "odd" space symmetry of the triplet state. Take for example diatomic H_2 that shares two electrons as shown in Figure 15.9B. The even symmetry of the singlet allows the electrons to become closer together while the triplet does the opposite, which would energetically favor the triplet. It should be noted that wavefunctions become increasingly complex as atoms gain more electrons and form molecules. As a result there is no simple rule about the ordering of the energies of excited states although one often hears "triplets are lower in energy than singlets". While this is often the case, especially for organics, in reality nothing is assured pending a full quantum chemical analysis.

Tipping the energy balance between high spin triplet states and low spin singlets due to the exchange interaction has many significant effects. For one, if an excited organic molecule intersystem crosses into a triplet state it will vigorously react with oxygen as O_2 is also triplet. Furthermore, the unpaired electron configuration of a high spin state imparts magnetic properties such as ferromagnetism. This phenomenon occurs when the constituent atoms of a solid piece of metal align their magnetic moments in parallel, which massively augments the high spin magnetic character. This is due to the strength of the exchange interaction, which is a function of atomic geometry because of the unusual nature of the exchange integral. This is why some metals are magnetic and some are not; the crystal structure and interatomic distances of some materials don't allow for enough exchange to impart a net magnetic field.

15.6.4 Spin-orbit mixing, intersystem crossing and phosphorescence. Any molecular dynamics that require a change of the overall spin state is formally not allowed, and such processes are usually referred to as "spin forbidden". However, the spin-orbit effect relaxes this prohibition. For example, most molecules have singlet ground states, and as such upon absorption of light the final state must also be a singlet due to the spin selection rule. This is also consistent with the fact that a photon does not have any spin-type angular momentum. Once an excited state singlet is created, however, the spin-orbit effect allows that state to intersystem cross into the lower energy triplet as shown in Figure 15.10A. This is because the forbidden nature of the transition is lifted by spin-orbit coupling, which mixes the spin states together as shown in Figure 15.10B. Here, spin-orbit coupling rotates a triplet state eigenvector into the singlet electronic state space causing it to gain some singlet character. The same is true for the singlet, and as a result an excited singlet state can become a triplet given that it already has some triplet character. Phosphorescence, which is the emission of light from an excited triplet state back to a ground singlet state, is also allowed due to the spin-orbit effect.

15.7: Appendix

Triplets. A triplet wavefunction is defined by the Slater determinate: $\Psi^3\left(1,2\right)=$

det\frac{1}{\sqrt{2}}\left|{\mathit{\Psi}}_1\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_1\left(2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_2\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_2\left(2\right)\alpha \left(2\

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}$ as follows:

\[\int{}

ParseError: invalid DekiScript (click for details)

^3\left(1,2\right)\cdot \partial \tau = \nonumber \]

$$\int\left\{\psi_1^*\left(1\right)\alpha^*\left(1\right)\psi_2^*\left(2\right)\alpha^*\left(2\right)-\psi_2^*\left(1\right)\alpha^*\left(1\right)\psi_1^*\left(2\right)\alpha^*\left(2\right)\right\}\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left\{\Psi_1\left(1\right)\alpha\left(1\right)\Psi_2\left(2\right)\alpha\left(2\right)\right.$$
$$\left.-\Psi_2\left(1\right)\alpha\left(1\right)\Psi_1\left(2\right)\alpha\left(2\right)\right\}\cdot\partial\tau$$

Next the expression is FOIL'ed out and the spin wavefunctions are factored out:

\[\frac{1}{2}\int{}{\psi }^*_1\left(1\right){\mathit{\Psi}}_1\left(1\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}

ParseError: invalid DekiScript (click for details)

_2\left(2\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right)+\frac{1}{2}\int{}{\mathit{\Psi}}^*_1\left(2\right){\mathit{\Psi}}_1\left(2\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}^*_2\left(1\right){\mathit{\Psi}}_2\left(1\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right)-\frac{1}{2}\int{}{\mathit{\Psi}}^*_1\left(1\right){\mathit{\Psi}}_1\left(2\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}^*_2\left(2\right){\mathit{\Psi}}_2\left(1\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right)-\frac{1}{2}\int{}{\mathit{\Psi}}^*_1\left(2\right){\mathit{\Psi}}_1\left(1\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}^*_2\left(1\right){\mathit{\Psi}}_2\left(2\right)\cdot \partial \tau \int{}{\alpha }^*\left(1\right)\alpha \left(1\right)\int{}{\alpha }^*\left(2\right)\alpha \left(2\right) \nonumber \]

Since $\int\alpha^*\alpha=1$ and $\Psi_1^*\left(1\right)\Psi_1\left(1\right)=\left|\Psi_1\left(1\right)\right|^2$ etc., the above can be factored into:

$$\frac{1}{2}\left(\int\left|\Psi_1\left(1\right)\right|^2\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left|\Psi_2\left(2\right)\right|^2\cdot\partial\tau+\int\left|\Psi_1\left(2\right)\right|^2\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left|\Psi_2\left(1\right)\right|^2\cdot\partial\tau\right)$$
$$-\frac{1}{2}\left(\int\Psi_1^*\left(1\right)\Psi_1\left(2\right)\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\Psi_2^*\left(2\right)\Psi_2\left(1\right)\cdot\partial\tau+\int\Psi_1^*\left(2\right)\Psi_1\left(1\right)\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\Psi_2^*\left(1\right)\Psi_2\left(2\right)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary, and the integral results are the same. The result is the Coulomb integral minus the exchange integral:

\[\int{}

ParseError: invalid DekiScript (click for details)

^3\left(1,2\right)\cdot \partial \tau = \nonumber \]

$$\int\left|\Psi_1\left(1\right)\right|^2\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left|\Psi_2\left(2\right)\right|^2\cdot\partial\tau-\int\Psi_1^*\left(1\right)\Psi_1\left(2\right)\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\Psi_2^*\left(2\right)\Psi_2\left(1\right)\cdot\partial\tau$$

Singlets: A singlet wavefunction is defined by two Slater determinates:

det\frac{1}{2}\left(\left|{\mathit{\Psi}}_1\left(1\right)\alpha \left(1\right)\ {\mathit{\Psi}}_1\left(2\right)\alpha \left(2\right)\ {\mathit{\Psi}}_2\left(1\right)\beta \left(1\right)\ {\mathit{\Psi}}_2\left(2\right)\beta \left(2\right

$$=\frac{1}{2}\Psi_1\left(1\right)\alpha\left(1\right)\Psi_2\left(2\right)\beta\left(2\right)-\frac{1}{2}\Psi_2\left(1\right)\beta\left(1\right)\Psi_1\left(2\right)\alpha\left(2\right)-\frac{1}{2}\Psi_1\left(1\right)\beta\left(1\right)\Psi_2\left(2\right)\alpha\left(2\right)+\frac{1}{2}\Psi_2\left(1\right)\alpha\left(1\right)\Psi_1\left(2\right)\beta\left(2\right)$$

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}$ as:

\[\int{}

ParseError: invalid DekiScript (click for details)

^1\left(1,2\right)\cdot \partial \tau \nonumber \]

The expression is FOIL'ed and the spin wavefunctions are factored out on the following page. Since $\int\alpha^*\alpha=1$, $\int\alpha^*\beta=\int\beta^*\alpha=0$ and $\psi_1^*\left(1\right)\Psi_1\left(1\right)=\left|\Psi_1\left(1\right)\right|^2$ etc., half the terms can be removed, and the remainder factored into:

$$\frac{1}{2}\left(\int\left|\Psi_1\left(1\right)\right|^2\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left|\Psi_2\left(2\right)\right|^2\cdot\partial\tau+\int\left|\Psi_1\left(2\right)\right|^2\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left|\Psi_2\left(1\right)\right|^2\cdot\partial\tau\right)$$
$$+\frac{1}{2}\left(\int\psi_1^*\left(1\right)\Psi_1\left(2\right)\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\psi_2^*\left(2\right)\Psi_2\left(1\right)\cdot\partial\tau+\int\psi_1^*\left(2\right)\Psi_1\left(1\right)\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\psi_2^*\left(1\right)\Psi_2\left(2\right)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary. Thus, we have the Coulomb integral plus the exchange integral:

\[\int{}

ParseError: invalid DekiScript (click for details)

^1\left(1,2\right)\cdot \partial \tau = \nonumber \]

$$\int\left|\Psi_1\left(1\right)\right|^2\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\left|\Psi_2\left(2\right)\right|^2\cdot\partial\tau+\int\Psi_1^*\left(1\right)\Psi_1\left(2\right)\frac{e^2}{4\pi\varepsilon_0\left|r_1-r_2\right|}\Psi_2^*\left(2\right)\Psi_2\left(1\right)\cdot\partial\tau$$

which proves that the paramagnetic triplet state is lower in energy than the singlet.

```
\frac{1}{4}\int{}{\mathit{\Psi}}^*_1\left(1\right){\mathit{\Psi}}^*_2\left(2\right)\frac{e^2}{4\pi {\varepsilon }_0\left|r_1-r_2\right|}{\mathit{\Psi}}_1\left(1\right){\mathit{\Psi}}_2\left(2\right)\cdot \partial \tau \int{}{\al
```

Index

Glossary

Sample Word 1 | Sample Definition 1

Detailed Licensing

Overview

Title: Free Energy 1e (Snee)

Webpages: 95

Applicable Restrictions: Noncommercial

All licenses found:

- CC BY-NC 4.0: 93.7% (89 pages)
- Undeclared: 6.3% (6 pages)

By Page

- Free Energy 1e (Snee) - *CC BY-NC 4.0*
    - Front Matter - *CC BY-NC 4.0*
        - TitlePage - *CC BY-NC 4.0*
        - InfoPage - *CC BY-NC 4.0*
        - Table of Contents - *Undeclared*
        - Licensing - *Undeclared*
        - Acknowledgments - *Undeclared*
        - Forward - *Undeclared*
    - 1: Gas Equations of State - *CC BY-NC 4.0*
        - 1.1: Units and the Perfect Gas Law - *CC BY-NC 4.0*
        - 1.2: Van der Waals Equation - *CC BY-NC 4.0*
        - 1.3: The Virial Equation - *CC BY-NC 4.0*
        - 1.4: Phase Transitions - *CC BY-NC 4.0*
        - 1.5: Corresponding States - *CC BY-NC 4.0*
    - 2: Energy - *CC BY-NC 4.0*
        - 2.1: Work and the Inexact Differential - *CC BY-NC 4.0*
        - 2.2: Reversible and Irreversible Transitions - *CC BY-NC 4.0*
        - 2.3: Exact and Inexact Partials and Euler's Test - *CC BY-NC 4.0*
        - 2.4: Internal Energy (U) and the Equipartition Theorem - *CC BY-NC 4.0*
        - 2.5: Heat Transactions, Heat Capacity, and Adiabatic Systems - *CC BY-NC 4.0*
    - 3: Enthalpy, Legendre Transforms, and Thermodynamic Proofs - *CC BY-NC 4.0*
        - 3.1: Enthalpy and Changing Functions - *CC BY-NC 4.0*
        - 3.2: Heat Capacities - *CC BY-NC 4.0*
        - 3.3: Natural Variables and Legendre Transforms - *CC BY-NC 4.0*
        - 3.4: The Joule and Joule-Thomson Experiments - *CC BY-NC 4.0*
    - 4: Entropy and the 2nd Law - *CC BY-NC 4.0*
        - 4.1: Introduction to Entropy - *CC BY-NC 4.0*
        - 4.2: Entropy inside and outside- The 2nd Law and the Clausius Inequality - *CC BY-NC 4.0*
        - 4.3: Calculating Entropy Changes - *CC BY-NC 4.0*
        - 4.4: The Car Engine and the Carnot Cycle - *CC BY-NC 4.0*
        - 4.5: Refrigeration - *CC BY-NC 4.0*
        - 4.6: Maxwell Relationships - *Undeclared*
    - 5: Helmholtz and Gibbs Energy - *CC BY-NC 4.0*
        - 5.1: Helmholtz Energy (and The Clausius Inequality Pt. II) - *CC BY-NC 4.0*
        - 5.2: Gibbs Energy - *CC BY-NC 4.0*
        - 5.3: Calculations- Numerical and Derivations - *CC BY-NC 4.0*
        - 5.4: Advanced Derivations - Maxwell Relationships II - *CC BY-NC 4.0*
    - 6: Chemical Thermodynamics - *CC BY-NC 4.0*
        - 6.1: Entropy and the 3rd Law - *CC BY-NC 4.0*
        - 6.2: Energy, it's all relative - *CC BY-NC 4.0*
        - 6.3: Enthalpy and Gibbs Energy of Formation- Hess's Law examples - *CC BY-NC 4.0*
        - 6.4: Chemical reactions and chemical potential - *CC BY-NC 4.0*
        - 6.5: Equilibrium Constants - *CC BY-NC 4.0*
    - 7: Solutions and Colligative Properties - *CC BY-NC 4.0*
        - 7.1: Partial Vapor Pressure - *CC BY-NC 4.0*
        - 7.2: Partial Pressure Measurements and Raoult's Law - *CC BY-NC 4.0*
        - 7.3: Excess Functions and Ideal Solutions - *CC BY-NC 4.0*
        - 7.4: Henry's Law, Activity, and Ideal-Dilute Solutions - *CC BY-NC 4.0*
        - 7.5: Colligative Properties - *CC BY-NC 4.0*
    - 8: Phase Changes - *CC BY-NC 4.0*
        - 8.1: The Gibbs Phase Rule - *CC BY-NC 4.0*
        - 8.2: Entropy is the Reason Phase Changes Occur - *CC BY-NC 4.0*