Free Energy

by Preston T. Snee

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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 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.

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 $P \propto {}^{1}/_{V}$ 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

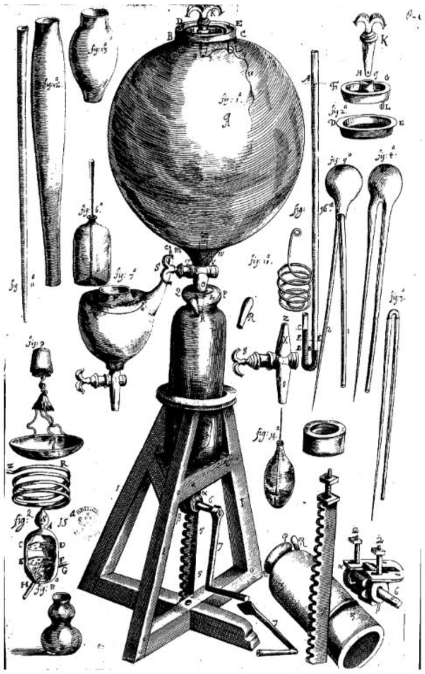


Figure 1.1. Boyle’s air pump and other measuring equipment.

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:

$$\mathrm{PV} \sim \mathrm{nT}$$

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: $\frac{\mathrm{kg \cdot m}}{\mathrm{s^2}}$, then the Pascal is: $\frac{\mathrm{kg \cdot m}}{\mathrm{s^2}} \cdot \frac{1}{\mathrm{m^2}} = \frac{\mathrm{kg}}{\mathrm{s^2 \cdot m}}$. When pressure is multiplied by volume in units of $\mathrm{m^3}$ the result is in Joules: $\mathrm{PV} = \frac{\mathrm{kg \cdot m^2}}{\mathrm{s^2}}$, which is energy. But nT is in units of mole·Kelvin, *which is not a Joule*. Thus, the equation: $\mathrm{PV} \sim \mathrm{nT}$ 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 $\frac{\mathrm{J}}{\mathrm{mol \cdot K}}$:

$$\mathrm{PV} = \mathrm{nRT} \tag{1.1}$$

In the SI system the gas constant is specifically $\mathrm{R} = 8.314 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$. 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:

- The left and right sides of an equation must have the same units.
- Terms in a sum must have the same units. For example, in the equation: $\mathrm{a} \pm \mathrm{b} = \frac{1}{\mathrm{c}}$, "a" and "b" have the same units.
- 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 π or 2.0 have no units at all.

Getting back to task, does $\mathrm{PV} = \mathrm{nRT}$ 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 $\mathrm{PV} = \mathrm{nRT}$ a "perfect" equation? I think not- and here is how you can tell. You

Example Problem 1.0

Problem: The Dieterici equation of state is: $P = \frac{RT \cdot e^{-a/RTV_m}}{(V_m - b)}$. What are the units of the "a" and "b" constants?

Answer: First, you can consider that the entire term: $\frac{RT \cdot e^{-a/RTV_m}}{(V_m - b)}$ must have units of pressure as P is on the left. However, it is easier to note that $(V_m - b)$ is a sum and thus "b" has the same units as V_m: m^3/mol. Last, you should know that the argument of an exponential cannot have units; thus $\frac{a}{RTV_m}$ is unitless. This means that "a" must have the same units as RTV_m, which is $\frac{J}{mol \cdot K} \cdot K \cdot \frac{m^3}{mol} = \frac{J \cdot m^3}{mol^2}$.

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:

$$P = \frac{nRT}{V - n \cdot b} - \frac{n^2 \cdot a}{V^2} \tag{1.2}$$

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.

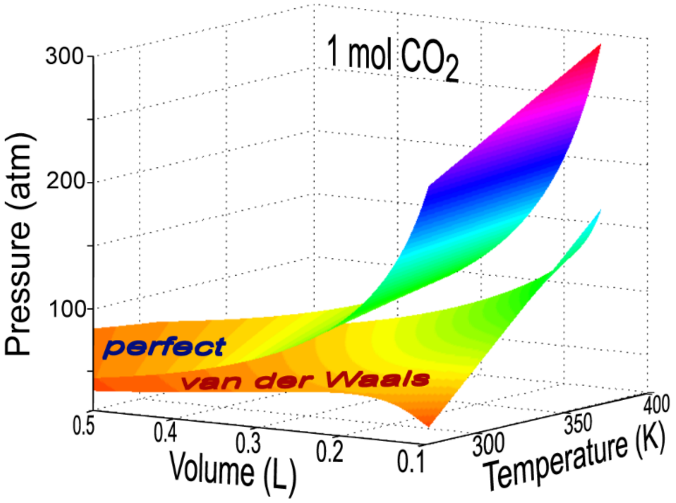


Figure 1.2. Pressure vs. volume and temperature for CO_2 gas demonstrates that the real gas pressure is less than the perfect gas pressure.

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
CH_4	225.3	0.04278	45.0	188
CO_2	364.0	0.04267	73.1	304
H_2O	553.6	0.03049	218	647

Table 1.0. Van der Waals "a" and "b" parameters can be used to calculate the gas phase critical points. These are very closely matched to the experimental values.

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:

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

Based on the previous discussion, hopefully you realize the Joule doesn't matter, rather the $\mathrm{n \cdot b}$ 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:

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

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

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

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

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

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 $\lim_{P \to \infty \text{ Pa}} \frac{nRT}{\left(P + \frac{a \cdot n^2}{V^2}\right)} = \frac{nRT}{(\infty + \infty)} = 0 \text{ m}^3$, and thus:

$$\lim_{P \to \infty \text{ Pa}} (V - n \cdot b) = 0 \text{ m}^3$$

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":

$$Z = \frac{P_{\text{real}}}{P_{\text{perfect}}} = \frac{P_{\text{real}}V}{nRT} \tag{1.3}$$

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 $P_{\text{real}}V$ 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.

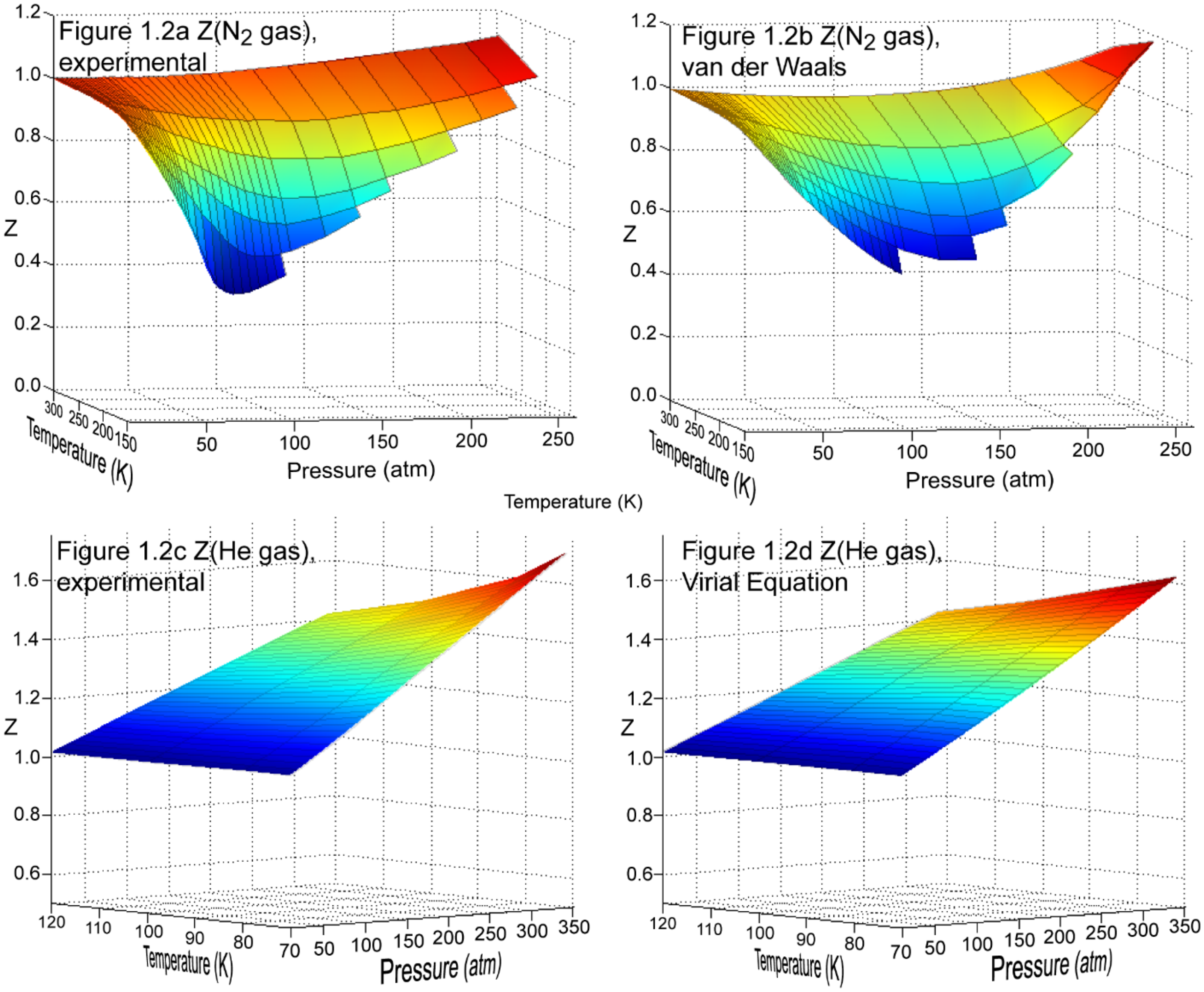


Figure 1.3. A. Compression factor (Z) vs. nominal pressure and temperature for N_2 gas. **B**. Z as predicted for N_2 by the van der Waals equation. **C**. Z for He gas reveals very different behavior compared to N_2. **D**. Z derived from the Virial Equation reveals good accuracy due to the temperature dependence of the Virial's parameters.

The 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 $\frac{V}{nRT}$:

$$\frac{PV}{nRT} = Z = \frac{V}{V - n \cdot b} - \frac{a}{RTV} \tag{1.4}$$

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

Example Problem 1.1

Problem: a. If 1 mol of CH_4 gas in 0.0983 dm^3 has a temperature of -82.59 ºC at 45.99 bar, is it is behaving like a perfect gas? **b.** Is the van der Waals equation more accurate?

Answer: a. There are several ways to do this, but they all involve calculating a parameter from the perfect gas law and showing it doesn't match the result above. If you went with pressure, you should have shown that:

$P = \frac{\mathrm{nRT}}{\mathrm{V}} = \frac{1\ \mathrm{mol} \times 8.314\ \mathrm{J/K/mol} \times (273.15-82.59)\ \mathrm{K}}{0.0983\ \mathrm{L}} = 16117\ \mathrm{kPa}$, which is 161.17 bar and significantly higher than the experimental result.

You can also show that R is not 8.314 J/K/mol via:

$45.99\ \mathrm{bar} = 4599\ \mathrm{kPa} = \frac{\mathrm{nRT}}{\mathrm{V}} = \frac{1\ \mathrm{mol} \times \mathrm{R} \times (273.15-82.59)\ \mathrm{K}}{0.0983\ \mathrm{L}}$; this makes R = 2.37 J/K/mol, which is way off. You could likewise do this with the number of moles or volume, either way, the perfect gas law does not describe the condition above.

b. The equation is: $P = \frac{\mathrm{RT}}{\mathrm{V_m - b}} - \frac{\mathrm{a}}{\mathrm{V_m^2}}$, with V_m = 0.0983 dm^3 / 1 mol = 0.0983 dm^3/mol and the other parameters can be found in the book or the internet:

$P = \frac{8.314\ \mathrm{J/K/mol} \times (273.15-82.59)\mathrm{K}}{0.0983\mathrm{L/mol} - 0.04278\ \mathrm{L/mol}} - \frac{2.283 \frac{\mathrm{bar \cdot L^2}}{\mathrm{mol^2}} \cdot \left(\frac{100\ \mathrm{kPa}}{\mathrm{bar}}\right)}{(0.0983\ \mathrm{L/mol})^2} = 4909.5\ \mathrm{kPa} = 49.1\ \mathrm{bar}$. This is clearly much closer to the actual pressure than that from the perfect gas law.

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 "b" 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 $\frac{n}{V}$:

$$\frac{PV}{nRT} = 1.0 + B(T) \cdot \left(\frac{n}{V}\right) + C(T)\left(\frac{n}{V}\right)^2 + \cdots \tag{1.5}$$

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 ~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.:

$$\text{res. volume} = \lim_{V_m \to \infty\ m^3/mol} \left(V_{m,real} - V_{m,perf}\right) \tag{1.6}$$

The reason that a limit is applied (either P→0 Pa or $V_m \to \infty$ 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 $\lim_{V_m \to \infty m^3/mol} \left(\frac{PV_m}{RT}\right) = 1.0$. However, what about the difference $\lim_{V_m \to \infty\ m^3/mol} \left(V_m - \frac{RT}{P}\right)$? 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 eq. 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:

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

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

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

And apply the limit as follows:

$$\lim_{V_m \to \infty\ m^3/mol} \left(V_m - \frac{RT}{P}\right) = \lim_{V_m \to \infty\ m^3/mol} \left(B(T) \cdot \left(\frac{RT}{PV_m}\right) + C(T) \frac{RT}{PV_m^2}\right)$$

Now here we have a problem. If $V_m \to \infty$ 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 $\lim_{V_m \to \infty\ m^3/mol} \left(\frac{PV_m}{RT}\right) = 1.0$, which means we can replace every PV_m with RT:

$$\text{res. volume} = \lim_{V_m \to \infty\ m^3/mol} \left(B(T) \cdot \left(\frac{RT}{RT}\right) + C(T) \frac{RT}{RT \cdot V_m}\right) = B(T)$$

Since the RT term is not affected by the limit of increasing volume or equivalently decreasing pressure, the $B(T)$ term survives while the $C(T)$ 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.

Example Problem 1.2

Problems: a. The Dieterici equation of state: $P = \frac{RT\cdot e^{-a/RTV_m}}{(V_m - b)}$ is another real gas equation with positive "a" and "b" constants. Can you derive the equation for the compression factor?

b. If a gas that follows the Dieterici equation of state has $a = 0$ and $b = 0$, it would be a perfect gas. In that case what is the compression factor equal to?

Answer: a. First multiply by $(V_m - b)$ and divide by P:

$$V_m - b = \frac{RT \cdot e^{-a/RTV_m}}{P}$$

and bring the "b" over to the right side:

$$V_m = \frac{RT \cdot e^{-a/RTV_m}}{P} + b$$

Next, multiply by $\frac{P}{RT} = \frac{1}{V_m^0}$ to get $Z = \frac{V_m}{V_m^0}$ on the left side as so:

$$V_m \cdot \left(\frac{P}{RT}\right) = \frac{V_m}{V_m^0} = \frac{RT \cdot e^{-a/RTV_m}}{P} \cdot \left(\frac{P}{RT}\right) + b \cdot \left(\frac{P}{RT}\right) = e^{-a/RTV_m} + b \cdot \frac{P}{RT}$$

b. If $a = 0$ then $e^{-a/RTV_m} = 1$ and $b = 0$ makes the $b \cdot \frac{P}{RT}$ term goes away, leaving Z=1.0 which is true for a perfect gas.

Since we are here discussing residual volume, how about we use the van der Waals equation for the same purpose? Starting with eq. 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:

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

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:

$$\lim_{V_m \to \infty \, m^3/mol} \left(V_m - \frac{RT}{P}\right) = \text{res. volume} = \lim_{V_m \to \infty \, m^3/mol} \left(b - \frac{a}{PV_m} - \frac{a \cdot b}{PV_m^2}\right)$$

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

$$\text{res. volume} = \lim_{\mathrm{V_m \to \infty\ m^3/mol}} \left(\mathrm{b} - \frac{\mathrm{a}}{\mathrm{RT}} - \frac{\mathrm{a \cdot b}}{\mathrm{RTV_m}} \right) = \mathrm{b} - \frac{\mathrm{a}}{\mathrm{RT}} \tag{1.7}$$

Thus $\frac{\mathrm{a \cdot b}}{\mathrm{PV_m^2}} \to 0$ as $\mathrm{V_m} \to \infty$. 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 °C and the bottom one is -8.9 °C). Do you see how the green line at 30.9 °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. $\frac{\partial \mathrm{P}}{\partial \mathrm{V_m}} = 0\ \mathrm{atm \cdot mol/L}$. In fact, its true that the double derivative is also flat: $\frac{\partial^2 \mathrm{P}}{\partial \mathrm{V_m}^2} = 0\ \mathrm{atm^2 \cdot mol^2/L^2}$. Setting these two derivatives equal to 0 provides two equations that can be used to solve the two unknowns, which are the critical pressure $P_c = \frac{\mathrm{a}}{27\mathrm{b}^2}$ 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 $T_c = \frac{8\mathrm{a}}{27\mathrm{R \cdot b}}$.

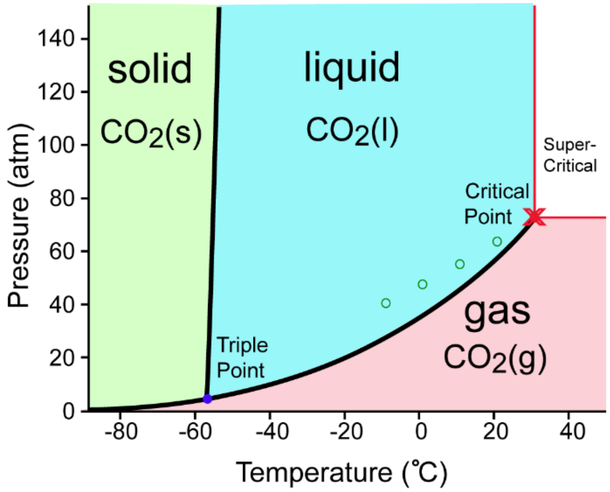


Figure 1.4. The phase diagram of CO_2 shows the solid, liquid, gas, and critical regions as a function of pressure and temperature. The triple and critical points occur at (5.2 atm, 216.6 K) and (72.9 atm, 304.3 K) , respectively.

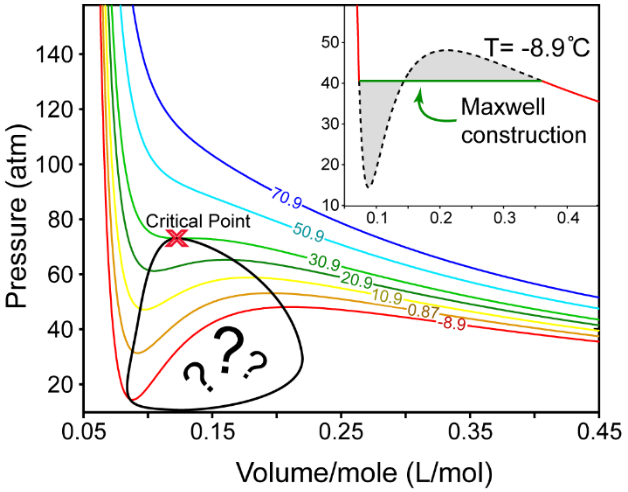


Figure 1.5. Diagram of P vs. V_m for CO_2 as predicted by the van der Waals equation. Note how P increases with V_m at certain points. This is because CO_2 has liquified. Inset: A Maxwell construction is where liquids and gases coexist.

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 °C. To understand, imagine that we have a container at -8.9 °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:

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

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:

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

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

which is further reduced into:

$$P^* = \frac{8T^*}{3V^* - 1} - \frac{3}{V^{*2}} \qquad (1.8)$$

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

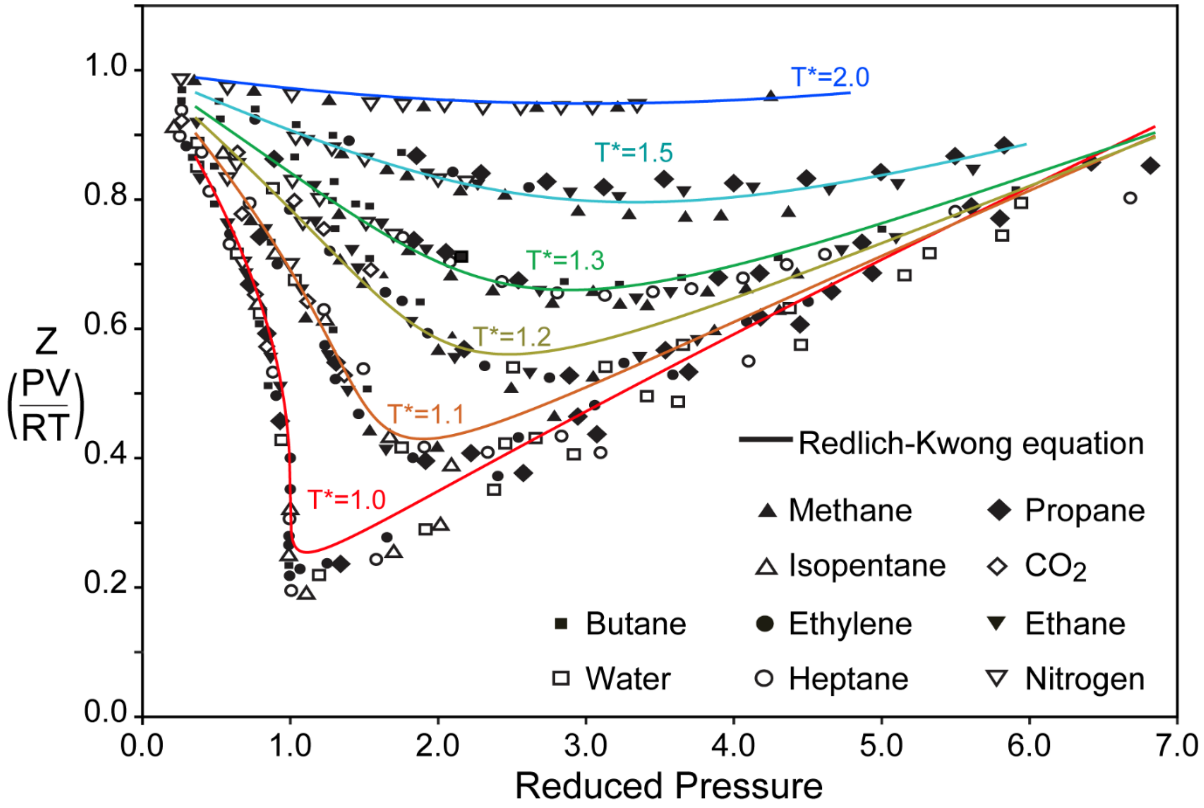


Figure 1.6. Compression factor (Z) as a funciton of reduced pressure and temperature for several gases and the theoretical prediciton based on the Redlich-Kwong equation of state. The data clustering reveal that gases interact in fundamentally similar ways.

reproduce the data shown in Figure 1.6. Instead, we have used the Redlich-Kwong equation of state:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T} \cdot V_m(V_m + b)} \tag{1.9}$$

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.

References

[1] 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.

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

Problems: Numerical

1. The Hindenburg exploded because it was full of H_2 gas which caught on fire; nearly two Olympic swimming pools worth of water were created in the blast. The reaction is: $O_2 + 2H_2 \rightarrow 2H_2O$. On a smaller scale, let's say 1 mol O_2 and 4 mol H_2 react to completion in a 11.2 L reaction vessel maintained at a 25 ˚C. What is the pressure **a.** before and **b.** after the reaction runs to completion? Assume perfect gas behavior. **(10 pts)**

2. Let's rework question 1 with 1 mol O_2 and 1 mol H_2, in a 22.4 L reaction vessel maintained at 25 ˚C. What is the pressure **a.** before and **b.** after I let the reaction run to completion? Assume perfect gas behavior. **(10 pts)**

3. a. It was found through experiment that a balloon of O_2 gas with a mass of 1.6 g in a 15.4 cm^3 volume exerts a pressure of 71.44 atm at 10 ºC. Does oxygen behave like a perfect gas? **(5 pts)**

b. Use the van der Waals equation of state to solve the pressure of O_2. In this example, you should find that the perfect gas and van der Waals equations' results are very similar. This is because real gas equations are more important when a gas is under extreme conditions; the next few problems will illustrate this. **(5 pts)**

4. a. It was found through experiment that a balloon of Xe gas with a mass of 262 g in a 0.82 dm^3 volume exerts a pressure of 36.03 atm at -0.15 ˚C. Does xenon behave like a perfect gas? **(5 pts)**

b. Use the van der Waals equation of state to solve the pressure of Xe. **(5 pts)**

c. What are the relative errors of the perfect gas and van der Waals results compared to the known pressure? Hint: relative error is $\frac{\Delta P}{P} \times 100\%$. **(5 pts)**

5. a. Calculate the pressure of two moles of H_2 gas with 1.0 dm^3 volume at 25 ˚C using the perfect gas law. **(5 pts)**

b. Now do the same using the van der Waals equation. **(5 pts)**

c. I believe that the van der Waals pressure is higher than the perfect gas result- what drives up the pressure, the van der Waals "a" or "b" parameter? Prove your assertations via calculation. **(10 pts)**

6. **a.** I looked up the fact that 1 mol of CH_4 gas in a 0.0983 dm^3 volume exerts a pressure of 45.99 bar at -82.59 ºC. Does methane behave like a perfect gas? **(5 pts)**

b. Is the van der Waals equation more accurate? **(5 pts)**

c. You should have found that the van der Waals equation more accurate. Why is that? Hint: calculate the van der Waals pressure without the finite volume "b" correction and again without the attractive force "a" component. If you find that removing one of them creates more error then when removing the other, then that parameter is the most important. **(10 pts)**

7. a. It was found through experiment that a balloon of CO_2 gas with a mass of 47.0 g in a 0.22 dm^3 volume exerts a pressure of 100.6 atm at 86.85 ˚C. Does CO_2 behave like a perfect gas? **(5 pts)**

b. Use the van der Waals equation of state to solve the pressure of CO_2 in the example above (the constants are in the Handout section. Also, show all work, including cancellation of units!). **(5 pts)**

c. Why is the van der Waals equation more accurate? **(10 pts)**

Hint: calculate the van der Waals pressure without the finite volume "b" correction and again without the attractive force "a" component. If you find that removing one of them creates more error then when removing the other, then that parameter is the most important.

8. If N_2 gas is in a container which I expand by half the original volume to a total of 4 dm^3 isothermally (at constant temperature). The pressure is now 6 bar, what was the original pressure before expansion? You can use any units you like, assume perfect gas behavior, and show your work! **(5 pts)**

9. If N_2 gas is in a container which I expand by half the original volume to a total of 9 dm^3 isothermally (at constant temperature). The pressure is now 12 bar, what was the original pressure before expansion? You can use any units you like, assume perfect gas behavior, and show your work! **(5 pts)**

10. If N_2 gas is in a container which I contract by one third of the original volume to a total of 12 dm^3 isothermally (at constant temperature). The pressure is now 2 bar, what was the original pressure before the contraction? You can use any units you like, assume perfect gas behavior, and show your work! **(5 pts)**

11. If N_2 gas is in a container which I compress by one third of the original volume to a total of 1.0 dm^3 isothermally (at constant temperature). The pressure is now 1 bar, what was the original pressure before the compression? You can use any units you like, assume perfect gas behavior, and show your work! **(5 pts)**

12. I have detected an unknown perfect gas in the breath of a cat. It appears to be made entirely of sulfur and fluorine. The density of the gas was measured to be 6.12 g/L at 17.6 °C and at a pressure of 101.325 kPa. What is the molecular formula of this cat gas? Hint: assume perfect gas behavior, and the formula is something like SF_x. **(7 pts)**

13. I have detected another unknown perfect gas in the breath of a cat. It appears to be made entirely of carbon and oxygen. The density of gas (1.769 g/L) was measured in a warm room (30 °C) and at a pressure of 101.325 kPa. What is the molecular formula of this cat gas? Hint: the gas is a well-known troublesome molecule! **(7 pts)**

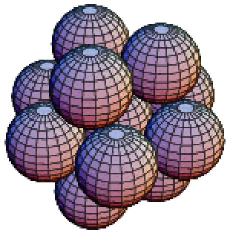
14. I have detected yet another unknown perfect gas in the breath of a cat. It appears to be made entirely of xenon and fluorine. At room temperature (25 °C) and pressure (101.325 kPa) the density of the gas is 10.026 g/L. What is the molecular formula of this cat gas? **(7 pts)**

Hint: It's hard to imagine a molecule with more than one xenon atom in it.

15. I have detected yet another unknown perfect gas in the breath of a cat. It appears to be made entirely of germanium and chlorine (what has this cat been up to!). At 30 °C and at a pressure of 101.325 kPa the density of the gas is 8.619 g/L. What is the molecular formula of this cat gas? Note: The molecule only has one germanium atom in it.

(7 pts)

16. The atomic radius of xenon is 108 pm. Is that consistent with its "b" parameter of 5.105×10^{-2} L/mol? Hint: what is the volume of a mole of xenon atoms and how does that compare to the "b" parameter? Double hint: a picometer is 1×10^{-12} m. **(5 pts)**



17. It may not be fair to compare the volume of an atom to the "b" parameter as there must be some "in-between" space when packing a mole of atoms as close as possible. This may make the volume of the "b" parameter appear a bit over ~10× greater than the volume of the atom. For instance, in the hexagonal close pack structure shown here, the volume taken up by a sphere of radius r is: $V_{hcp} = 8\times\pi\times r^3$. Can you now show that the volume of hexagonally close packed xenon atoms is only about ~40% less than the "b" parameter (meaning that they are actually pretty similar)?

(5 pts)

18. a. The van der Waals equation of state predicts the residual volume of a real gas is: $\lim_{P\to 0}(V_m - V_m^0) = b - \frac{a}{RT}$. If this gas was actually a perfect gas, can you tell me what is the value of "a" that makes this true? Hint: it should be a function of b, R, and T, and you do know what the residual volume of a perfect gas is, don't you? **(4 pts)**

b. Take the "a" and "b" constants of nitrogen, and calculate how "a" compares to b·RT at 160 °C. Now do the same for helium. Explain why this explains why nitrogen is very perfect gas-like and helium is not. ***Be very careful about units!*** For example, a Joule·Liter/mol^2 is the same as kPa·Liter^2/mol^2! **(4 pts)**

Problems: Theoretical or Explain in Words

1. If: $\text{🐴} = e^{-\text{🐈}}$ and: $F(\text{🐓}) = \frac{\text{🐓}^2}{\text{🐴}}\ln(\text{🐓})$

What is: **a.** $\frac{\partial F}{\partial \text{🐓}}$ **b.** $\frac{\partial F}{\partial \text{🐴}}$ **c.** $\frac{\partial F}{\partial \text{🐈}} = \frac{\partial F}{\partial \text{🐴}}\frac{\partial \text{🐴}}{\partial \text{🐈}}$ **(6 pts)**

2. What is the following definite integral? $\int_0^r 4\pi\,\text{🐓}^2\,\partial\text{🐓}$ **(5 pts)**

3. Tell me whether the following are extensive or intensive: **(5 pts)**

a) Temperature **b)** R×T **c)** k_B **d)** R×moles **e)** 🐐/mol **f)** 🐐

Hint: R is the gas constant 8.314 J/K/mol k_B is the Boltzmann constant (1.38×10^{-23} m^{2}kgK^{-1}s^{-2}). The goat represents the number of goats.

4. Why is R ×T intensive? **(3 pts)**

5. Why do you think all van der Waals "a" and "b" constants are positive? **(4 pts)**

6. a. Why does methane have a larger van der Waals "b" term (0.04278L/mol) compared to the same of helium (0.0237 L/mol)? **(3 pts)**

b. Why does methane have a larger van der Waals "a" term (2.283 L^2 bar/mol^2) compared to the same of helium (0.03457 L^2 bar/mol^2)? **(3 pts)**

Hint: both are due to some molecular properties; you should name it specifically.

7. a. Why does hydrogen have a much smaller van der Waals "a" term (0.2476 L^2 bar/mol^2) compared to the same of xenon (4.250 L^2 bar/mol^2)? **(3 pts)**

b. Why does hydrogen have a smaller van der Waals "b" term (0.02661 L/mol) compared to the same of xenon (0.05105 L/mol)? **(3 pts)**

Hint: both are due to some molecular properties; you should name it specifically.

8. The van der Waals (equation 1.2): $P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$, the attractive forces that lower the pressure are not as powerful when the volume is large. Why does that make sense? **(4 pts)**

9. In the Virial (equation 1.5): $PV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right)$, what are the units of B and C (and prove it). Hint: start with this: $PV_m = RT + \frac{RT \times B}{V_m} + \frac{RT \times C}{V_m^2}$. **(4 pts)**

10. The van der Waals equation of state is: $P = \frac{nRT}{(V-b)} - \frac{an^2}{V^2}$ and the Berthelot equation of state is: $P = \frac{nRT}{(V-b)} - \frac{an^2}{TV^2}$. Why do you think Berthelot added that factor of 1/T in the second term? **(2 pts)**

11. Calculate $\left.\frac{\partial V}{\partial T}\right)_P$ for the can der Waals equation of state, which is $P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$. Doesn't this look hard? After all, you can not write this function as V=… Perhaps the Euler chain formula can help: $\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$.

(10 pts)

12. Can you show that the van der Waals equation $P = \frac{nRT}{(V-nb)} - \frac{an^2}{V^2}$ can be approximated as: $\frac{nR}{P} = \frac{(V-nb)}{T} + \frac{an}{RT^2}$? You are going to need to remove terms $\propto \frac{1}{V^3}$ and insert the perfect gas equation as well. **(10 pts)**

13. Calculate $\left.\frac{\partial V_m}{\partial T}\right)_P$ for the Berthelot equation of state, which is: $P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$. Doesn't this look hard? After all, you can not write this function as V_m=… Perhaps the Euler chain formula can help: $\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$.

(10 pts)

14. The Berthelot constants "a" and "b" are always positive and very very small. Thus, $\left.\frac{\partial V_m}{\partial T}\right)_P$ is almost always positive given that: $\left.\frac{\partial V_m}{\partial T}\right)_P = -\frac{\frac{R}{V_m - b} + \frac{a}{T^2 V_m^2}}{\frac{-RT}{(V_m - b)^2} + \frac{2a}{TV_m^3}}$. Can you explain why the top term $\frac{R}{V_m - b} + \frac{a}{T^2 V_m^2}$ is probably going to be positive while the bottom term $\frac{-RT}{(V_m - b)^2} + \frac{2a}{TV_m^3}$ will almost always be negative? For example, is R ever negative? No, it's defined as positive; and therefore –R is always negative etc. **(5 pts)**

15. The Virial equation of state is: $PV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2}\right)$, where B and C are empirical constants. Can you calculate the residual volume = $\lim_{P \to 0}(V_m - V_m^0)$, where V_m^0 is the perfect gas volume per mol? Also don't forget $\lim_{P \to 0}\left(\frac{PV_m}{RT}\right) = 1$. **(5 pts)**

16. What is the compression factor for the Virial Equation of state? Hint: $Z = \frac{PV_m}{RT}$. **(5 pts)**

17. If $Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2}$ for the Virial equation of state, what would B have to be equal to for the gas to behave like a perfect gas? Hint: You do know what the compression factor of a perfect gas is, don't you? **(5 pts)**

18. a. It turns out that the compression factor of most gases is slightly below 1. Therefore, do you think the residual volume $\lim_{P \to 0}(V_m - V_m^0)$ is generally positive or negative? **(3 pts)**

b. I looked up the fact that most gases have Virial C parameters that are positive. Therefore, are the B parameters positive or negative? **(2 pts)**

c. Hydrogen and helium, being somewhat odd gases, generally have Z>1. Therefore, is their residual volume positive or negative? **(2 pts)**

19. I came up with my own equation of state. It works like: $\mathrm{V_m} = \frac{\mathrm{RT}}{\mathrm{P}} - \mathrm{b}$, where "b" is an empirical constant. Can you calculate the form of the compression factor $\mathrm{Z} = \frac{\mathrm{V_m}}{\mathrm{V_m^0}}$, where $\mathrm{V_m^0}$ is the perfect gas volume per mol? It should be a function of "b" and $\mathrm{V_m^0}$. **(5 pts)**

20. It turns out van der Waals was very careful when "designing" the van der Waals equation: $\mathrm{P} = \frac{\mathrm{RT}}{(\mathrm{V_m - b})} - \frac{\mathrm{a}}{\mathrm{V_m^2}}$. If you're not sure, let's see why he divided the "a" term by $\mathrm{V_m^2}$ and not $\mathrm{V_m}$. Specifically, can you calculate the residual volume of an alternative equation of state $\mathrm{P} = \frac{\mathrm{RT}}{(\mathrm{V_m - b})} - \frac{\mathrm{a}}{\mathrm{V_m}}$, and show that the residual volume is -∞ L/mol (which doesn't make sense)? **(7 pts)**

21. It turns out van der Waals was very careful when "designing" the van der Waals equation: $\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V_m - b}} - \frac{\mathrm{a}}{\mathrm{V_m^2}}$. If you're not sure, let's see why he divided the "a" term by $\mathrm{V_m^2}$ and not $\mathrm{V_m^3}$. Specifically, can you calculate the residual volume of an alternative equation of state: $\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V_m - b}} - \frac{\mathrm{a}}{\mathrm{V_m^3}}$ and show that the residual volume is "b", and that the "a" coefficient plays no role? **(7 pts)**

22. Calculate $\left.\frac{\partial \mathrm{V_m}}{\partial \mathrm{a}}\right)_{\mathrm{P}}$ for a van der Waals gas, ie. $\mathrm{P} = \frac{\mathrm{RT}}{(\mathrm{V_m - b})} - \frac{\mathrm{a}}{\mathrm{V_m^2}}$. Doesn't this look hard? After all, you can not write this function as $\mathrm{V_m}$=… Perhaps the Euler chain formula can help: $\left.\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} \left.\frac{\partial \mathrm{y}}{\partial \mathrm{z}}\right)_{\mathrm{x}} \left.\frac{\partial \mathrm{z}}{\partial \mathrm{x}}\right)_{\mathrm{y}} = -1$, or can be expressed as $\left.\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} = -\left.\frac{\partial \mathrm{z}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \left.\frac{\partial \mathrm{x}}{\partial \mathrm{z}}\right)_{\mathrm{y}}$, or even as $\left.\frac{\partial \mathrm{x}}{\partial \mathrm{y}}\right)_{\mathrm{z}} = -\frac{\left.{}^{\partial \mathrm{z}}/_{\partial \mathrm{y}}\right)_{\mathrm{x}}}{\left.{}^{\partial \mathrm{z}}/_{\partial \mathrm{x}}\right)_{\mathrm{y}}}$. **(7 pts)**

23. The van der Waals equation of state predicts the compression factor of a real gas is: $\mathrm{Z} = \frac{\mathrm{V_m}}{\mathrm{V_m - b}} - \frac{\mathrm{a}}{\mathrm{RTV_m}}$. If this gas was actually a perfect gas, can you tell me what "a" would have to equal? **(7 pts)**

24. Now let's see if we can derive an alternative expression for the compression factor for the van der Waals equation of state: $\mathrm{P} = \frac{\mathrm{RT}}{(\mathrm{V_m - b})} - \frac{\mathrm{a}}{\mathrm{V_m^2}}$. Can you show that: $\mathrm{Z} = \frac{\mathrm{PV_m}}{\mathrm{RT}} = 1 - \frac{\mathrm{a \cdot (V_m - b)}}{\mathrm{RTV_m^2}} + \frac{\mathrm{Pb}}{\mathrm{RT}}$? Hint: start by multiplying the left and right-hand sides by ($\mathrm{V_m}$ – b). **(7 pts)**

25. In the expression in question 24 above: $Z = \frac{\mathrm{PV_m}}{\mathrm{RT}} = 1 - \frac{\mathrm{a \cdot (V_m - b)}}{\mathrm{RTV_m^2}} + \frac{\mathrm{Pb}}{\mathrm{RT}}$, I contend that the last term $\frac{\mathrm{Pb}}{\mathrm{RT}}$ has all the units cancel. ***Without actually cancelling units***, prove it. A one sentence answer should suffice (use no mathematical expressions!). **(3 pts)**

26. Can you show that: $\mathrm{Z} = 1 + \frac{\mathrm{Pb}}{\mathrm{RT}} - \frac{\mathrm{a(V_m - b)}}{\mathrm{RTV_m^2}}$ can be approximated as $\mathrm{Z} \approx 1 + \frac{\mathrm{Pb}}{\mathrm{RT}} - \frac{\mathrm{aP}}{(\mathrm{RT})^2} + \cdots$ if you substitute in the perfect gas equation $\mathrm{P} = \frac{\mathrm{RT}}{\mathrm{V_m}}$ into the 3rd term? **(7 pts)**

27. Can you show that, for the van der Waals equation: $\mathrm{V_m} \approx \frac{\mathrm{RT}}{\mathrm{P}} + \mathrm{b} - \frac{\mathrm{a}}{\mathrm{RT}} + \cdots$

using: $\mathrm{Z} = \frac{\mathrm{PV_m}}{\mathrm{RT}} \approx 1 + \frac{\mathrm{Pb}}{\mathrm{RT}} - \frac{\mathrm{aP}}{(\mathrm{RT})^2}$? **(5 pts)**

28. Here is a new real gas equation: $V_m = \frac{RT}{P} + \frac{aRT}{P\cdot(V_m - b\cdot V_m)}$. Can you show that the residual volume is: $\lim\limits_{P\to0}\left(V_m - \frac{RT}{P}\right) = \frac{a}{1-b}$? **(7 pts)**

29. The Dieterici equation of state is: $P = \frac{RT\cdot e^{-a/RTV_m}}{(V_m-b)}$. Please show that this reduces to the perfect gas law if a=0 and b=0. **(6 pts)**

30. Calculate $\left.\frac{\partial V_m}{\partial T}\right)_P$ for the Dieterici equation of state, which is: $P = \frac{RT\cdot e^{-a/RTV_m}}{(V_m-b)}$. Doesn't this look hard? After all, you cannot write this function as V_m=… Perhaps the Euler chain formula can help: $\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1.$

(10 pts)

31. I found that the Dieterici equation of state reduces to the perfect gas law if a=0 and b=0. Thus, the derivatives do as well. Thus, can you show that: $\left.\frac{\partial V_m}{\partial T}\right)_P = -\frac{\frac{R\cdot e^{-a/RTV_m}}{(V_m-b)} + \frac{aRT\cdot e^{-a/RTV_m}}{RV_mT^2(V_m-b)}}{\frac{a\cdot e^{-a/RTV_m}}{V_m^2(V_m-b)} - \frac{RT\cdot e^{-a/RTV_m}}{(V_m-b)^2}}$ for the the Dieterici equation of state returns the perfect gas law result if you set a=0 and b=0? **(8 pts)**

32. a. The Dieterici equation of state: $P = \frac{RT\cdot e^{-a/RTV_m}}{(V_m-b)}$ has a compression factor of $Z = \frac{V_m}{V_m^0} = e^{-a/RTV_m} + b\frac{P}{RT}$, where the constants a and b are always positive. Can you show that this is correct? **(5 pts)**

b. If a gas that follows the Dieterici equation of state had a=0 and b=0, it would be a perfect gas. Is that case what is the compression factor Z equal to? **(2 pts)**

33. For a real gas that follows this equation of state: $V - nb = \frac{nRT}{P}e^{-a/P}$, can you solve the following derivatives?

a. $\left.\frac{\partial V}{\partial T}\right)_P$ **b.** $\left.\frac{\partial V}{\partial P}\right)_T$ **c.** $\left.\frac{\partial P}{\partial V}\right)_T$ **(15 pts)**

Hint: For pt. c, you might want to use a variant of the Euler chain formula: $\left.\frac{\partial x}{\partial y}\right)_z = \frac{-1}{\left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y}$? Also don't try to simply it, pt. c is 10 miles long.

Chapter 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):

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

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 $\mathrm{mc^2}$, which describes how nuclear reactors generate electricity? Actually, $\mathrm{mc^2}$ 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 that 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 Changes of energy: work and heat. Now that we are content with measuring changes in energy, we can start by defining it with:

$$\partial\mathrm{U} = \partial\mathrm{w} + \partial\mathrm{q} \tag{2.2}$$

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: $\int_{0\ \mathrm{mol}}^{\mathbf{n}\ \mathrm{mol}} \partial \mathrm{n}$ physically corresponds to leaking **n** moles of a gas into a vacuum chamber. Likewise integrating volume: $\int_{0\ \mathrm{m}^3}^{\mathrm{X\ m}^3} \partial \mathrm{V}$ 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, $\partial \mathrm{n} \sim 0$ mol and $\partial \mathrm{V} \sim 0\ \mathrm{m}^3$, 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.

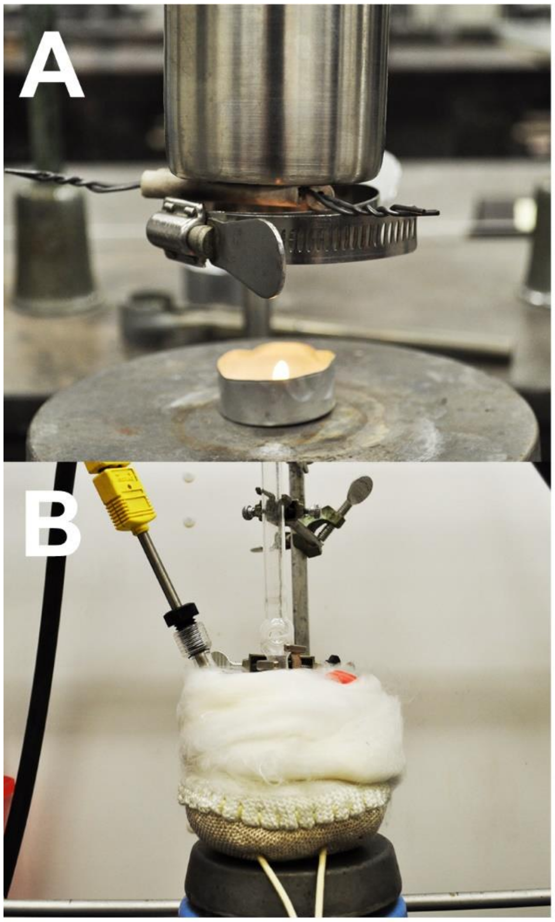


Figure 2.1. A. An example of inefficient (or irreversible) heating. **B.** Thermal insulation guarantees an efficient (or reversible) transfer of heat.

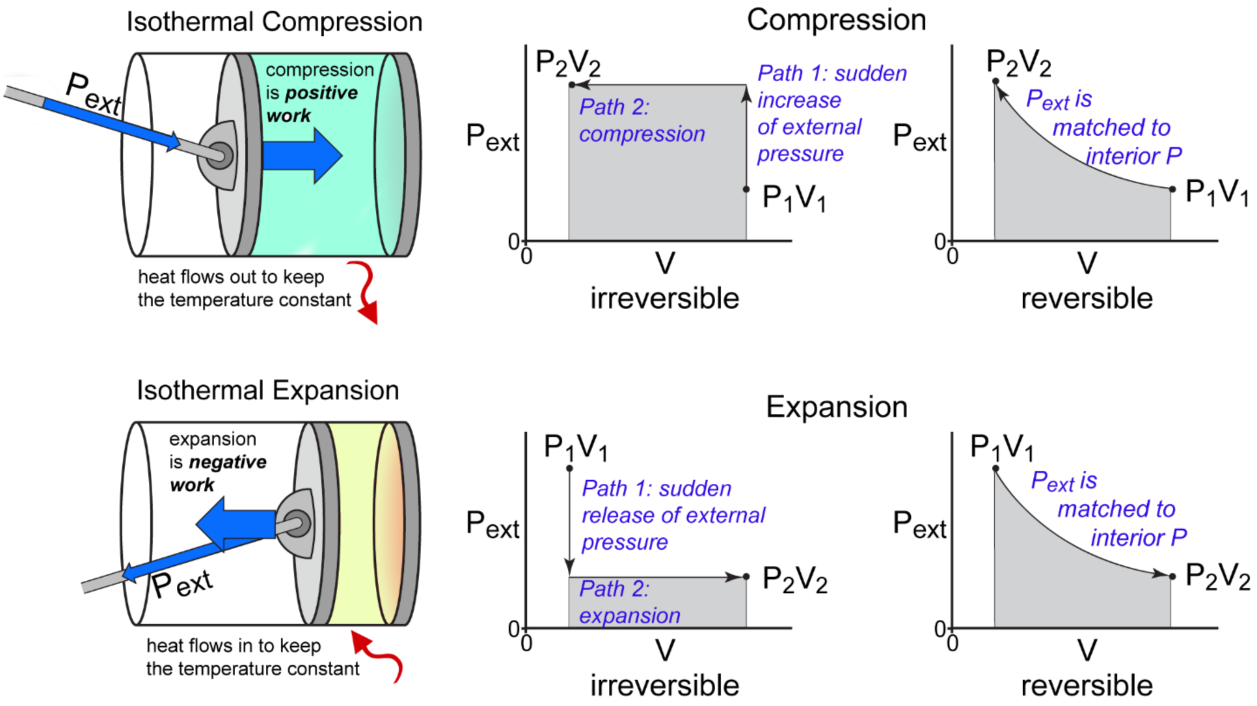


Figure 2.2. A piston compressing (top) or expanding (bottom) as they take either the reversible or irreversible path. The work can be calculated from the P vs. V diagrams.

2.2 Work, and the inexact differential. 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:

$$\partial w = -P_{ext} \cdot \partial V \tag{2.3}$$

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: $\partial \mathrm{w} = -\mathrm{P}_{\mathrm{ext}} \cdot \partial \mathrm{V}$ has two partials (∂w and ∂V), we need to integrate both to define a finite, measurable value for work:

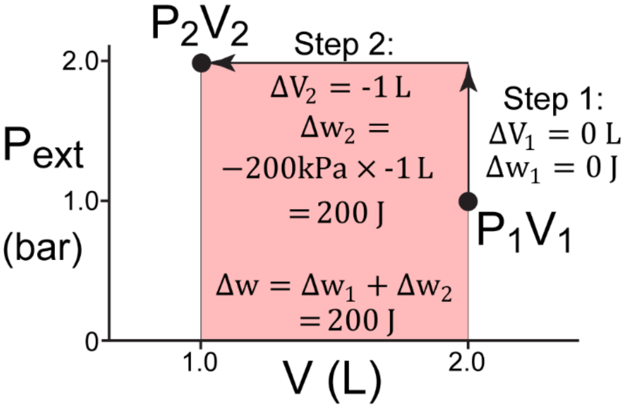


Figure 2.3. An irreversible compression can be analyzed in two steps.

$$\int \partial \mathrm{w} = \Delta \mathrm{w} = \int -\mathrm{P}_{\mathrm{ext}} \cdot \partial \mathrm{V} \qquad (2.4)$$

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:

$$\Delta \mathrm{w}_1 = \int_{2\mathrm{L}}^{2\mathrm{L}} -\mathrm{P}_{\mathrm{ext}} \cdot \partial \mathrm{V} = -\mathrm{P}_{\mathrm{ext}} \times (2\mathrm{L} - 2\mathrm{L}) = 0\ \mathrm{J}$$

There is no work done in the 1st step because it doesn't matter what the pressure is doing if it gets multiplied by $\Delta \mathrm{V}_1 = 0$ L. Now the second step where the volume does change the work is integrated as:

$$\Delta \mathrm{w}_2 = -\mathrm{P}_{\mathrm{ext}} \int_{2\mathrm{L}}^{1\mathrm{L}} \partial \mathrm{V} = -200\ \mathrm{kPa}\ \times (1\mathrm{L} - 2\mathrm{L}) = +200\ \mathrm{J}$$

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: $V = 2L \cdot \frac{100\ \text{kPa}}{P_{\text{ext}}}$. 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: $P_{\text{ext}} = 100\ \text{kPa} \cdot \frac{2\ L}{V}$ because the exterior pressure explicitly appears in the equation for work: $\partial w = -\boldsymbol{P_{ext}} \cdot \partial V$. 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:

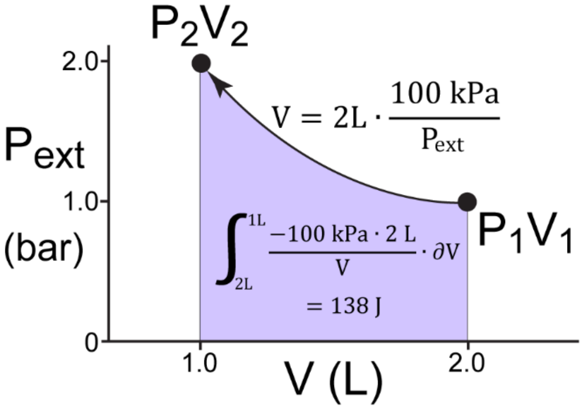


Figure 2.4. An reversible compression creates more negative work.

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

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: $\int x^{-1}\, \partial x = \ln(x)$:

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

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.

2.3 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:

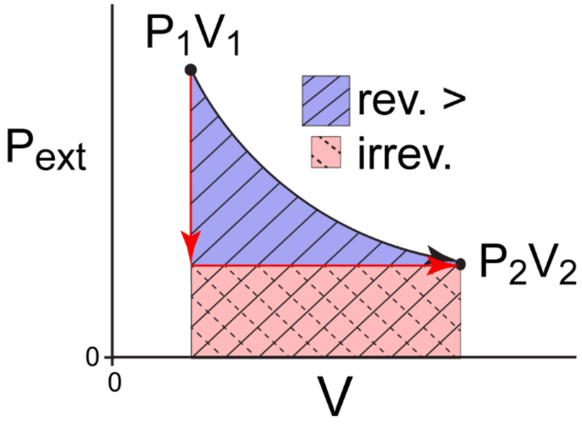


Figure 2.5. Reversible work area (blue single hatch) is greater than the irreversible (red cross hatch).

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

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

$$\Delta w_{rev} = -nRT\cdot\int_{V_i}^{V_f}\frac{\partial V}{V} = -nRT\cdot\ln\left(\frac{V_f}{V_i}\right) \tag{2.5}$$

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:

$$\Delta w_{irrev} = -P_{ext} \cdot \int_{V_i}^{V_f} \partial V = -P_{ext} \cdot \Delta V \tag{2.6}$$

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

2.4 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(x) is $\frac{\partial f}{\partial x}$; however, when the function has two or more variables, i.e. $f(x, y)$, we must analyze the change in the function with respect to both x and y as: $\partial f(x, y) \approx \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}$. 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: $\partial f(x, y) \approx \left.\frac{\partial f}{\partial x}\right)_y + \left.\frac{\partial f}{\partial y}\right)_x$. However, this expression can’t be fully correct as ∂f has the same units as the function f while $\left.\frac{\partial f}{\partial x}\right)_y$ 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.

Example Problems

Problem 2.1: 0.1 mol of N_2 gas at a constant 25 °C at 100 kPa is compressed by 200 kPa exterior pressure isothermally and irreversibly. What is the work done?

Answer: First note that we are doing an irreversible compression, and since we know the exterior pressure, we just have to calculate the initial and final volumes. Here we will assume that $P_iV_i = nRT$, and thus $V_i = \frac{nRT}{P_i} = \frac{0.1\ \text{mol}\cdot 8.314\frac{J}{K\cdot\text{mol}}\cdot(25+273)\ K}{100\ \text{kPa}} = 2.48$ L. Likewise the final volume is $V_f = \frac{P_iV_i}{P_f}$ =1.24 L. Thus, the work is:

$\Delta w_{irrev} = -P_{ext}\cdot\Delta V = -200\ \text{kPa}\cdot(1.24\ \text{L} - 2.48\ \text{L}) = +248$ J.

Problem 2.2: 1.24 L of 0.1 mol of N_2 gas at a constant 25 °C at 200 kPa expands against 100 kPa external pressure isothermally and irreversibly. What is the work done?

Answer: The initial conditions in this problem are set to the same as at the end state of the previous problem. As a result, you can be assured that the final volume is 2.48 L, and the work is: $\Delta w_{irrev} = -100\ \text{kPa}\cdot(2.48\ \text{L} - 1.24\ \text{L})$ = -124 J. The sum of the work in from problem 1 (+248 J) and the work out from this example (-124 J) don't negate each other. This results in irreversibility, which you will later learn in Chapter 4 creates entropy.

Problem 2.3: 0.1 mol of N_2 gas at a constant 25 °C at 100 kPa is compressed to a final pressure of 200 kPa isothermally and reversibly. What is the work done?

Answer: Note that we are doing the reversible version of problem 1 above. As a result, the starting and ending volumes are the same; however, the work is different:

$\Delta w_{rev} = -nRT\cdot\ln\left(\frac{V_f}{V_i}\right) = -0.1\ \text{mol}\cdot 8.314\frac{J}{K\cdot\text{mol}}\cdot 298\ K\cdot\ln\left(\frac{2.48L}{1.24L}\right) = 171$ J.

Problem 2.4: 0.1 mol of N_2 gas at a constant 25 °C at 200 kPa expands to 100 kPa final pressure isothermally and reversibly. What is the work done?

Answer: The starting point here is the end point of problem 3, and the expansion will result in a doubling of the volume just as in the irreversible case. However, the work will be a greater negative amount of energy compared to the irreversible expansion as determined by:

$\Delta w_{rev} = -nRT\cdot\ln\left(\frac{V_f}{V_i}\right) = -0.1\ \text{mol}\cdot 8.314\frac{J}{K\cdot\text{mol}}\cdot 298\ K\cdot\ln\left(\frac{1.24\ L}{2.48\ L}\right) = -171$ J. Thus, the work in problems 3 & 4 cancel each other, as though no work had been performed at all!

The solution is that the real partial is:

$$\partial f(x,y) = \left.\frac{\partial f}{\partial x}\right)_y \partial x + \left.\frac{\partial f}{\partial y}\right)_x \partial y \tag{2.7}$$

which is tantamount to calculating a change in the function (∂f) by following $f(x,y)$ 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 $f(x,y) = x \cdot y$ is:

$$\partial f(x,y) = \left.\frac{\partial x \cdot y}{\partial x}\right)_y \partial x + \left.\frac{\partial x \cdot y}{\partial y}\right)_x \partial y = y \cdot \partial x + x \cdot \partial y \tag{2.8}$$

This is an example of an exact differential, which means that there is a function $f(x,y)$ associated with $\partial f(x,y)$. 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.

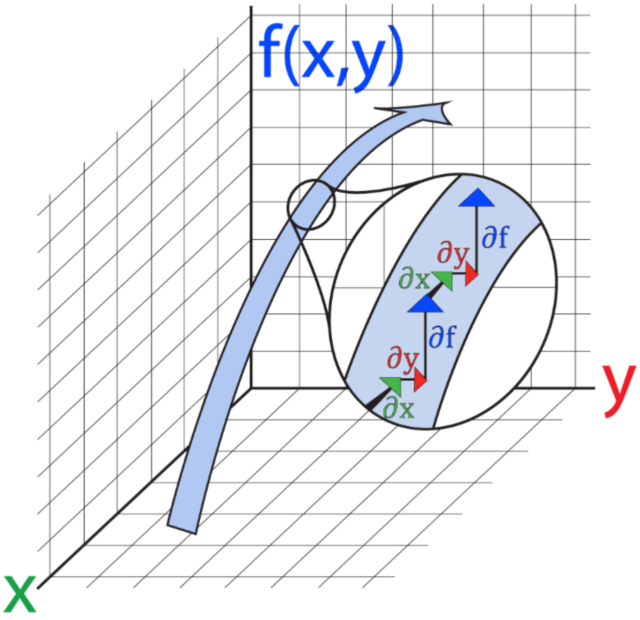


Figure 2.6. How to visualize the partial change of a multivariable function.

Inexact differentials are the opposite of the exact. An example is: $\partial f(x,y) = x \cdot \partial y$. This is ~1/2 the exact differential in eq. 2.8, and as a result you could never write a function $f(x,y)$ that could be differentiated into $\partial f = x \cdot \partial y$. Work: $\partial w(P_{ext}, V) = -P_{ext} \cdot \partial V$ is clearly inexact because it is identical to: $\partial f(x,y) = x \cdot \partial y$, 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 $\partial \mathrm{f}(\mathrm{x}, \mathrm{y})$ is exact or not:

$$\frac{\partial}{\partial \mathrm{y}} \frac{\partial \mathrm{f}}{\partial \mathrm{x}}\bigg)_{\mathrm{y}}\Bigg)_{\mathrm{x}} = \frac{\partial}{\partial \mathrm{x}} \frac{\partial \mathrm{f}}{\partial \mathrm{y}}\bigg)_{\mathrm{x}}\Bigg)_{\mathrm{y}} \tag{2.9}$$

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 $\partial \mathrm{w}$ and $\partial \mathrm{q}$ are inexact differentials, but first we need to introduce energy.

2.5 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 $\partial \mathrm{U}$ is exact. Since $\partial \mathrm{U}$ is exact then there must be an equation for U, and there is:

$$\mathrm{U} = \frac{1}{2} \mathrm{k_B T} \cdot (\text{degrees of freedom}) \tag{2.10}$$

where $\mathrm{k_B} = \frac{\mathrm{R}}{\mathrm{N_A}}$, which you can think of as the perfect gas constant for a single molecule. Equation 2.10 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: $\mathrm{U_m} = \frac{1}{2}\mathrm{RT} \cdot (\text{degrees of freedom})$, where $\mathrm{U_m}$ 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 $\frac{1}{2}\mathrm{k_B T}$. Thus, every molecule ought to have $3\mathrm{N} \cdot \frac{1}{2}\mathrm{k_B T}$ 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 $\mathrm{U_m} = \frac{3}{2}\mathrm{RT}$. 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 $\mathrm{U} = 3\mathrm{N} \cdot \frac{1}{2}\mathrm{k_B T}$ 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 $\sim\frac{5}{2}\mathrm{RT}$, not 3RT as expected, which means that one degree of freedom is not contributing to $\mathrm{U_m}$. 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

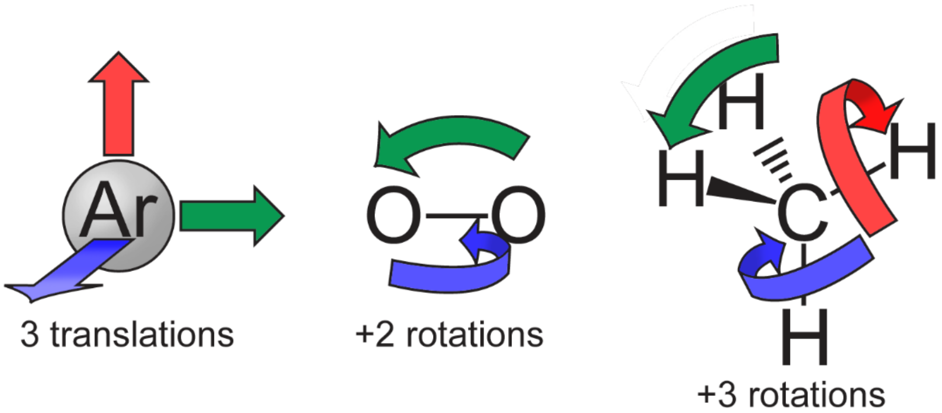


Figure 2.7. An atom has three degrees of translational freedom, a linear and a non-linear molecule has 2 and 3 extra rotational degrees of freedom, respectively.

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 $\frac{1}{2}k_BT$ 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
Ar	3 translational	3/2 RT 12.471 J/mol	3/2 RT 12.471 J/mol
O_2	3 translational, 2 rotational, 3×2-5 = 1 vibrational	3 RT 24.942 J/mol	5/2 RT 20.785 J/mol
CO_2	3 translational, 2 rotational, 3×3-5 = 4 vibrational	9/2 RT 37.413 J/mol	5/2 RT 20.785 J/mol
CH_4	3 translational, 3 rotational, 3×5-6 = 9 vibrational	15/2 RT 62.355 J/mol	3 RT 24.942 J/mol

Table 2.1. Internal energies of various gas phase molecules.

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 $\Delta\mathrm{U} = 0$ 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: $\partial\mathrm{U} = \frac{1}{2}\mathrm{k_B} \cdot (\text{degrees of freedom}) \cdot \partial\mathrm{T}$. Hence, if $\partial\mathrm{T} = 0$ K, then $\partial\mathrm{U} = 0$ 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 $\int \partial\mathrm{U} = 0$ J $= \Delta\mathrm{w} + \Delta\mathrm{q}$, then $\Delta\mathrm{q} = -\Delta\mathrm{w}$. 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 $\Delta\mathrm{q}$ 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 $\Delta\mathrm{q_{tot}} = \Delta\mathrm{q_1} + \Delta\mathrm{q_2}$ = 0 J? This is one reason why we call this process reversible.

2.6 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

Example Problem 2.5

Problem: 0.1 mol of N_2 gas at a constant 25 °C at 100 kPa is compressed by 200 kPa of external pressure irreversibly and is then suddenly released back to 100 kPa. What is the net Δq?

Answer: The conditions are the same as example problem 2.1, from which we see that the compression generated +248 J of work. This translates to –248 J of heat. Since the work is negative, heat flows ***out of the system***. In other words, the piston compresses and is hot at first, but it cooled down to room temperature by releasing heat. The subsequent irreversible expansion generates -124 J of work, which means that +124 J of heat goes into the system to warm it back to 25 °C. As a result, the net transformation resulted in:

$\Delta q_{tot} = \Delta q_1 + \Delta q_2$ = -124 J of heat out of the system.

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 ∂q and ∂T 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: $\left.\frac{\partial q}{\partial T}\right)_V = C_V$ and the other for constant pressure: $\left.\frac{\partial q}{\partial T}\right)_P = C_P$. 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: $\frac{\Delta q}{C_{P \text{ or } V}} = \Delta T$.

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

Table 2.2. Heat capacities of various gas phase molecules.

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 Δw = 0 J. The Equipartition theorem states that per molar internal energy: $U_m = \frac{1}{2}RT \cdot (\text{degrees of freedom})$ can only change with temperature:

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

which leads to:

$$C_{V,m} = \left.\frac{\partial q_m}{\partial T}\right)_V = \left.\frac{\partial U_m}{\partial T}\right)_V = \frac{1}{2}R \cdot (\text{degrees of freedom}) \cdot \left.\frac{\partial T}{\partial T}\right)_V$$

$$= \frac{1}{2}R \cdot (\text{degrees of freedom}) \qquad (2.11)$$

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

Example Problem 2.6

Problem: An insulated system has a wire filament inside of it with a power source attached. Please calculate the change in temperature of 1 bar O_2 gas at 25 °C when +124 J of thermal energy is added to the system, both at a constant 1 L volume and at constant pressure. Assume perfect gas behavior.

Answer: One of the tricks here is to note that you need moles of gas, but it isn't explicitly stated. However, using the perfect gas law with 100 kPa, 1 L at 25 °C gives us 0.04 moles of gas. Consequently the $C_V = 0.04\ \mathrm{mol}\ \times 21.1\ \mathrm{J/K/mol} =\ 0.85\ \mathrm{J/K}$. Likewise, $C_P = 1.186\ \mathrm{J/K}$. This gives us a rise in temperature at constant volume of $\Delta T = \Delta q/C_V = 124\ \mathrm{J}/0.85\ \mathrm{J/K} = 146\ \mathrm{K}$. Likewise, there is an increase of $105\ \mathrm{K}$ at constant pressure. One of the lessons here is that the constant volume condition has a higher temperature, because none of the heat energy was converted into work.

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.

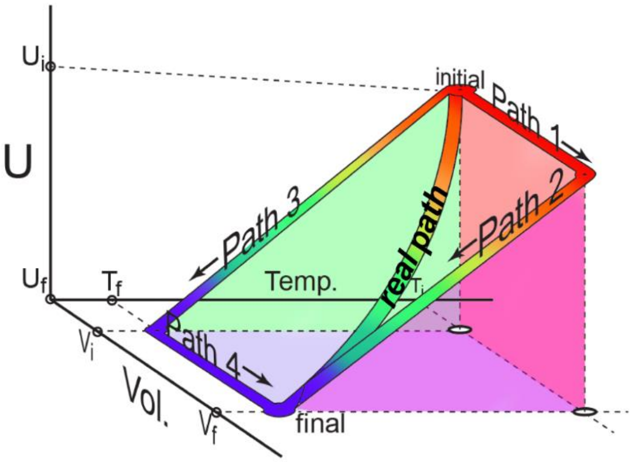
2.6.1 Adiabatic Systems. In our exploration of work it was found that compression adds energy into a system. This should cause the gas inside to heat up; however under isothermal conditions a heat transaction with the exterior kept the temperature constant. This heat transaction is expected if the piston 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 $\Delta U = \Delta w + \Delta q(0\ \mathrm{J}) = \Delta w$. 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 $\partial U = \partial w = -P\,\partial V$.



$$\Delta U_{tot} = \Delta U_1 + \Delta U_2$$
$$\Delta U_1 = 0\ J$$
$$\Delta U_2 = C_V \Delta T$$

or

$$\Delta U_{tot} = \Delta U_3 + \Delta U_4$$
$$\Delta U_3 = C_V \Delta T$$
$$\Delta U_4 = 0\ J$$

Figure 2.8. The change in internal energy of an adiabatic expansion can be calculated by decouping the process into separate paths. Regardless of whether the first step is a temperature or volume change, the internal energy difference is $U_f - U_i = C_V \times \Delta T$.

To connect $\partial\mathrm{U} = -\mathrm{P}\,\partial\mathrm{V}$ 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 $\partial\mathrm{U}$ 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 ($\Delta\mathrm{U}_1 = 0$ J). Path 2 represents a temperature change at constant volume, which makes $\Delta\mathrm{U}_2 = \mathrm{C_V}\Delta\mathrm{T}$ and thus $\Delta\mathrm{U_{tot}} = \Delta\mathrm{U}_1 + \Delta\mathrm{U}_2 = \mathrm{C_V}\Delta\mathrm{T}$. 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, $\Delta\mathrm{U_{tot}} = \mathrm{C_V}\Delta\mathrm{T}$ 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:

$$\mathrm{C_V}\,\partial\mathrm{T} = -\mathrm{P}\,\partial\mathrm{V} \tag{2.12}$$

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

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

This is important because we must integrate with respect to T and V (the partials in eq. 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 $\mathrm{T_f}$ to $\mathrm{T_i}$ on the left and $\mathrm{V_f}$ to $\mathrm{V_i}$ on the right:

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

After integration we find:

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

Now we can apply several identities for natural logs, such as: $-\ln\left(\frac{\mathrm{a}}{\mathrm{b}}\right) = \ln\left(\frac{\mathrm{b}}{\mathrm{a}}\right)$, as well as: $\mathrm{a}\cdot\ln(\mathrm{b}) = \ln(\mathrm{b^a})$ to make the following rearrangements:

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

and thus:

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

Example Problem 2.7

Problem: Please calculate the final volume, temperature, work done by 0.5 mol of a perfect gas, $C_{v,m}$ = 12.47 J/(K·mol), at 3 atm and 100 °C that reversibly and adiabatically expands against an outside pressure of 1 atm. What is the change in U?

Answer: We are generally seeking the final temperature using the adiabatic reversible equation of state: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$. However, we don't have initial and final volumes, although the initial volume can be found using $PV = nRT$, which is V_i=5.103 L. We can also manipulate the adiabatic equation of state to get the final volume as: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \left(\frac{P_fV_f}{P_iV_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$. Simplification gives: $\frac{P_fV_f}{P_iV_i} = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}}$. Further algebraic manipulation gives: $\frac{P_f}{P_i} = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}+1} = \left(\frac{V_i}{V_f}\right)^{\frac{C_V+nR}{C_V}}$. Plugging in numbers yields: $\frac{1\text{atm}}{3\text{atm}} = \left(\frac{5.103\text{L}}{V_f}\right)^{\frac{0.5\text{mol}\cdot(12.47+8.314\ \text{J/(K}\cdot\text{mol))}}{0.5\text{mol}\cdot 12.47\ \text{J/(K}\cdot\text{mol)}}}$. After some manipulation we get: $V_f = \frac{5.103\text{L}}{\left(\frac{1\text{atm}}{3\text{atm}}\right)^{\frac{0.5\text{mol}\cdot 12.47\text{J/(K}\cdot\text{mol)}}{0.5\text{mol}\cdot(12.47+8.314\ \text{J/(K}\cdot\text{mol))}}}}$ = 9.86 L. Now we can get the final temperature via: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$, which is: $\left(\frac{T_f}{373.15\text{K}}\right)^{\frac{0.5\text{mol}\cdot 12.47\ \text{J/(K}\cdot\text{mol)}}{0.5\text{mol}\cdot 8.314\ \text{J/(K}\cdot\text{mol)}}} = \frac{5.103\ \text{L}}{9.86\ \text{L}}$, yielding a T_f of 240.5 K. There is a slight shortcut that we could have used since we know P_f and V_f using the perfect gas law: gives $T_f = \frac{101.325\ \text{kPa}\cdot 9.86\text{L}}{0.5\text{mol}\cdot 8.314\ \text{J/(K}\cdot\text{mol)}}$ = 240.5 K; note that you may encounter rounding errors if you don't save the full variables in your calculator. Let's calculate the work using $\partial U = \partial w$, thus: $\int \partial w = \Delta w = n \cdot C_{V,m} \cdot \Delta T = 0.5\text{mol} \cdot 12.47\,\text{J/(K} \cdot \text{mol)} \cdot (240.3\text{K} - 373.15\text{K})$ =-828 J.

Taking the exponential of both sides results in:

$$\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f} \tag{2.13}$$

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

Example Problem 2.8

Problem: Let's rework problem 2.7 for an *irreversible* transition. Please calculate the final volume, temperature, work done by 0.5 mol of a perfect gas, $C_{v,m}$ = 12.47 J/(K·mol) and $C_{P,m}$ = 20.8J/(K·mol) at 3 atm and 100 °C that irreversibly and adiabatically expands against an outside pressure of 1 atm. What is the change in U?

Answer: Since PV = nRT for the initial and final states, we have $T_1 = \frac{P_1V_1}{nR}$ and $T_2 = \frac{P_2V_2}{nR}$. Knowing that n=0.5 mol, T_1=373.15 K, P_1 = 3 atm = 303.975 kPa, P_2 = 1 atm = 101.325 kPa we can calculate from the above that V_1 = 5.103 L. Now we need to know the volume and temperature of the final state (T_2, V_2) to calculate all the other thermodynamic variables, and while PV = nRT still works, we have a slight problem. This is because, although we know P_2, we simultaneously do not know V_2 nor T_2. Essentially, you have one equation with two unknown variables. However, $-P_{ext}\Delta V = C_V\Delta T$ can be used to resolve the problem. First, we redefine this as to address the size extensivity of heat capacity:

$$-P_{ext}(V_2 - V_1) = n \cdot C_{V,m}(T_2 - T_1)$$

Next, note that we can relate the final temperature to the final volume as:

$$-P_{ext}(V_2 - V_1) = n \cdot C_{V,m}\left(\frac{P_2V_2}{nR} - T_1\right)$$

The amazing thing: we have all the variables in this one equation defined except for V_2, which we can now calculate from:

$$-101.3\text{kPa} \cdot (V_2 - 5.103\text{L}) = 0.5\text{mol} \cdot 12.47\,\text{J}/(\text{K} \cdot \text{mol}) \cdot \left(\frac{101.3\text{kPa} \cdot V_2}{0.5\text{mol} \cdot 8.314\,\text{J}/(\text{K} \cdot \text{mol})} - 373.15\text{K}\right)$$

Solving this for V_2 gives a final volume of 11.2 L. Now we can calculate T_2 two different ways: If we use $\frac{P_2V_2}{nR}$, we get: $T_2 = \frac{101.3\text{kPa}\cdot 11.2\text{L}}{0.5\text{mol}\cdot 8.314\,\text{J}/(\text{K}\cdot\text{mol})} =$ 273.6 K. Or, we could have used: $-P_{ext}(V_2 - V_1) = n \cdot C_{V,m}(T_2 - T_1)$, which after we put in all the known variables is: $-101.3\text{kPa} \cdot (11.2\text{L} - 5.103\text{L}) = 0.5\text{mol} \cdot 12.47\,\text{J}/(\text{K} \cdot \text{mol}) \cdot (T_2 - 373.15\text{K})$, which makes T_2 = 273.6 K. It's the same no matter how we calculate it! The last thing is to calculate the work, which is $\Delta w = n \cdot C_{V,m} \cdot \Delta T = 0.5\text{mol} \cdot 12.47\,\text{J}/(\text{K} \cdot \text{mol}) \cdot (273.6\text{K} - 373.15\text{K}) =$ -621 J. This is also the change in internal energy.

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:

$$C_V\Delta T = -P_{ext}\Delta V \tag{2.14}$$

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.

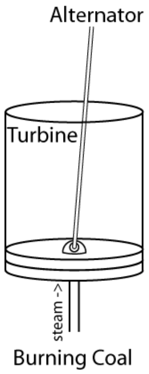
Conclusion. Thus far we have shown the basics of energy, heat and work, via the 1st Law of Thermodynamics. However, we still have much to learn before analyzing chemical processes; in fact, the content of this chapter uses gas expansion and contraction in place of chemical transformations because understanding 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.

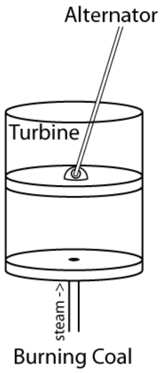
Problems: Numerical

1. The piston in a car engine has to push out the exhaust gas. To do so, it moves its 1 cm^2 surface area by 1.0 cm of length against an external pressure of 1 bar (that's the tailpipe pressure). How much work does this take? **(5 pts)**

2. The turbo-alternator in a coal-burning power plant generates AC electricity by rotating a bundle of wires through a magnetic field. The torque is provided by a turbine which itself is powered by steam generated by burning coal. Let's say that the turbine initially has no volume but is suddenly filled with a constant external pressure of steam (50 atm) that moves a 10 m^2 piston 20 m in length. How much work does this take? **(5 pts)**

3. Here we repeat question 2 for a turbine that initially has no volume. Quickly it is filled with steam at a constant external pressure of 100 atm that moves a 2-meter radius piston 7.86 m in length. How much work does this take? **(5 pts)**





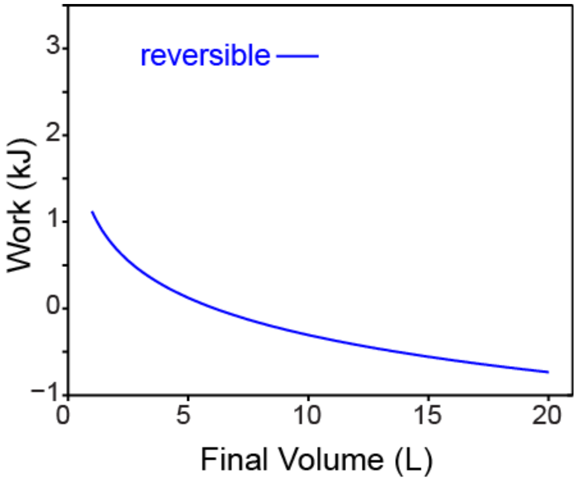
4. Power plants that burn fossil fuels emit "flue-gas". The flue-gas is at 10 MPa pressure in the power plant turbine, and then expands in the smokestack to 101.325 kPa as it is released to the atmosphere. The amount of energy the plant generates is 43 MJ per 1 m^3 of gas that comes out of the smokestack, and note that a typical power plant produces 1 GJ per second. Assuming that the flue-gas is at room temperature (25 °C), can you calculate n, Δq, Δw, and ΔU for the amount of gas that expands in the smokestack of a typical power plant in 1 second (**a**) reversibly (**b**) and irreversibly. Let's say that flue-gas is behaving like a perfect gas. **(8 pts)**

Hint: you know how much gas is released at the end of the process since I gave you T, P, and V.

5. When generating energy, the gas in the power plant turbine is initially at 600 °C. Let's say that there are 951 moles of a flue-gas (let's say it behaves like a perfect gas) and it must be cooled to 25 °C in the constant volume of the turbine before expelling it into the smokestack. If $C_{v,m}$ = 20.785 J/K/mol, calculate Δq, Δw, and ΔU. **(5 pts)**

6. Two morons where I grew up once threw a 10 kg chunk of sodium into the Eno River. When it hit the water, it exploded and shot back up into the air, over and over again for a few miles. Assuming that the pressure was 1 bar and 30 °C, how much work was done by the expanding gas that was created by the reaction of sodium and water? **(7 pts)**

7. College students should be able to graph data, so let's practice to show the work of a reversible vs. irreversible process. **a.** For a reversible process, work is: $\Delta w = -nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$. Let's say you have 0.25 mole of gas at a temperature of 298 K. The initial volume is 6.113 L. Please make a graph of work vs. final volume, which spans say 1 L to 20 L in 0.1 L increments. It should look something like the graph here. **(5 pts)**



b. On the same graph, plot the irreversible work:

$\Delta w = -P_{ext} \cdot (V_f - V_i)$. Note that the external pressure must match the final volume. For example, if the final volume is 20 L, then P_{ext} must be 31 kPa for PV=nRT to work. Thus, plot: $\Delta w = -\frac{nRT}{V_f} \cdot (V_f - V_i)$, where the final volume spans say 1L to 20 L in 0.1 L increments on the same graph in pt. a. **(5 pts)**

c. Which type of work is more negative and why? **(2 pts)**

8. Assume constant temperature: **a.** Calculate Δq, Δw, and ΔU for 0.1 mol of N_2 gas compressing from 1.0 L to 0.5 L at 304 K reversibly. **(6 pts)**

b. Calculate the same when the gas is compressed by a constant external pressure. **(6 pts)**

Hint for pt b. Now, why didn't I give you the external pressure? Do you not need to know it, or perhaps you do- just think about how you can cause a piston to compress with a constant external pressure. Why would the piston stop moving at 0.5L?

9. If I let gas in a piston expand by removing all external pressure, how much work is done? **(2 pts)**

10. Let's say I have 0.17 mol N_2 gas in a 3.6 L balloon at 25 °C. If I put it over a candle and add 56.7 J of heat energy, I will make the gas expand against a constant 1 atm of pressure; as a result it stays at a constant temperature. Please calculate Δq, Δw, ΔU, and ΔV. **(5 pts)**

11. What is the final pressure, temperature, and volume of xenon gas that doubles its volume reversibly and adiabatically starting from 1atm, 10.0 L at 25 °C? You might need to know that $C_{v,m}$ = 12.47 J/K/mol and $C_{p,m}$ = 20.79 J/K/mol. Assume perfect gas behavior. **(5 pts)**

12. It's cold outside and I am wearing a perfectly insulating jacket. As a result, when I slowly breathe out 3.7 L of N_2 g at 37 °C and 1 atm of pressure expands to 4.2 L reversibly and adiabatically. What is Δq, Δw, ΔU, ΔV and ΔT for this process? ($C_{p,m}$ = 29.1 J/K/mol and $C_{v,m}$ = 20.6 J/K/mol for N_2) (**6 pts**)

13. Assume isothermal conditions: For women, the average lung capacity is 4.2 L of air, and the average breath is 0.5 L. Knowing that air is mostly nitrogen, calculate Δq, Δw, and ΔU for:

a. 0.17 mol of N_2 gas compressing from 4.2 L to 3.7 L at 25 °C reversibly and, **(4 pts)**

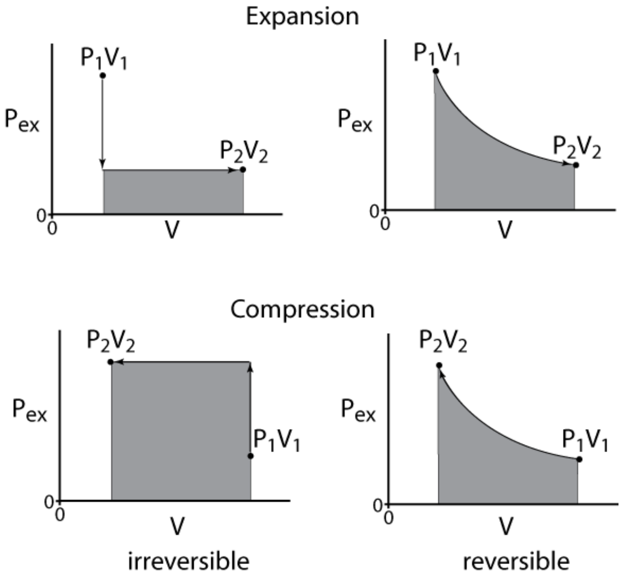
b. the same when the gas is compressed by a constant external pressure. Let's say that N_2 is behaving like a perfect gas. Assume that these changes occur before the gas escapes your lungs! In other words it's a closed system. **(4 pts)**

Hint for pt b. You need to know the constant external pressure, but I don't provide it. Or did I? After all, why would your lungs stop compressing at 3.7L of air? Is it because the external pressure is equal to the internal?

14. You can survive without special equipment under a pressure of about ~7 atm (its actually 704 kPa) while diving. Let's say you surface from 704 kPa and you expel 0.5 L of air into a final one atmosphere of pressure (101.3 kPa). The air in your lungs is 37 ºC, and it has a $C_{V,m}$ of 20.85 J/K/mol and $C_{P,m}$ = 29.19 J/K/mol, so what is Δq, n, C_P, T_f, C_V, ΔU, and Δw? The conditions are adiabatic and reversible, and please assume perfect gas behavior. **(8 pts)**

Hint: The ordering of variables requested isn't random. Also, $\frac{P_i}{P_f} = \left(\frac{T_i}{T_f}\right)^{\frac{C_P}{nR}}$, and the number of moles should be 0.1365 mol (please show this). Also note that the values are somewhat unrealistic- somewhat unphysical numbers are being used to make the calculations easier.

Problems: Theoretical or Explain in Words



1. Shown here is a P·V graph of a gas expanding (negative work), I can see that the area under the curve, the work energy, is greatest for the reversible process. This is consistent with the idea that a reversible process provides the most negative work.

a. However, there seems to be a problem when I compress a gas as shown here, where the irreversible process has the greatest area under the curve. Can you tell me how these graphs are still consistent with the fact that a reversible process provides the most negative work?

(5 pts)

b. Using the graph of expansion above, explain why expanding against no pressure (i.e. a vacuum) means no work is done. **(2 pts)**

c. How do I calculate the work energy created by a piston if I am pressing as hard as possible against it, but its jammed and unmovable? **(2 pts)**

2. a. Assume isothermal conditions: if the reversible work is the most negative work out of a system, reversible heat is the most positive heat. Why? **(2 pts)**

b. Assume isothermal conditions: if I reversibly do work on a system by expanding it then the heat Δq is +. Does the cylinder feel hot or cold when you touch it and why? **(2 pts)**

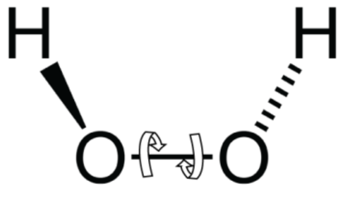
3. Here is a small table of molar heat capacities:

Chemical	$C_{v,m}$(J/K/mol)	$C_{p,m}$(J/K/mol)
Argon	12.5	20.8
N_2	20.6	29.0

a. Can you explain the trends in the data? (Hint: the numbers above may not agree perfectly with any simple theory you develop.) **(4 pts)**

b. Now if we add peroxide to the list:

Chemical	$C_{v,m}$(J/K/mol)	$C_{p,m}$(J/K/mol)
Peroxide	34.8	37.2



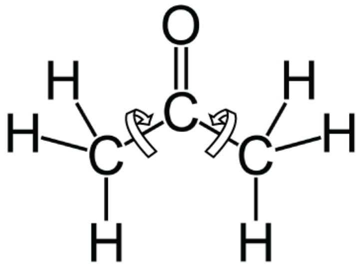
It appears that the internal energy of peroxide is ~8/2 RT, as opposed to 6/2 RT that we see for other non-linear molecules like methane. What do you think could be the extra degrees of freedom that peroxide has that methane doesn't? Here is a hint, look at the molecule to the right: **(4 pts)**

4. Here is a small table of heat capacities:

Chemical	$C_{V,m}$(J/K/mol)	$C_{P,m}$(J/K/mol)
Helium	12.5	20.8
O_2	20.6	29.0

a. Can you explain the trends in the data? (Hint: the numbers above may not agree perfectly with any simple theory you develop.) **(4 pts)**

b. If I added acetone to the list:



Chemical	$C_{V,m}$(J/K/mol)	$C_{P,m}$(J/K/mol)
Acetone	28.2	37.2

It appears that the internal energy of acetone is ~7/2 RT, as opposed to 6/2 RT that we see for other non-linear molecules. What do you think could be the extra degree of freedom that acetone has? Here is a hint, look at the molecule to the right. **(4 pts)**

5. When we learn more about entropy we will derive such relationships as: $\left.\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V}$. Can you re-derive the adiabatic equation of state: $\frac{P_f}{P_i} = \left(\frac{T_f}{T_i}\right)^{\frac{C_P}{nR}}$ from this relationship? Hint: you can ignore the constant "S" when you integrate the equation with respect to pressure and temperature. **(10 pts)**

6. a. I have two containers connected to each other by a valve. One has a gas at some pressure, the other is under vacuum. If I open the valve, what is the amount of work done by the gas expanding into the vacuum? **b.** If I enclose the whole thing in glass wool (i.e. I totally insulate it), what is the heat transferred? **c.** What is the change in internal energy in this example (expansion into a vacuum while the whole object is thermally insulated)? **(6 pts)**

7. a. Do you fly a kite under adiabatic or isothermal conditions? Please explain your answer. **b.** Most chemical reactions occur in solution. Generally, the chemicals are added to a solvent in a beaker that is open (but in a fume hood to keep you away from fumes). In a solvent under these conditions, do these chemical reactions occur under conditions of constant pressure or constant volume and why? **(4 pts)**

8. a. Do you ride your bike outside under adiabatic or isothermal conditions? Please explain your answer. **(4 pts)**

b. Normal cells use the mitochondria to generate ATP for energy; for every glucose molecule consumed, the mitochondria create 36 ATP molecules. Cancer cells use glycolysis, which produces 2 ATP molecules for every glucose consumed. It is very odd that cancer would use a less efficient process to create energy, and it causes further health problems beyond the cancer itself. Regardless, is this process occurring under conditions of constant pressure or constant volume? Please explain your answer. **(4 pts)**

9. I have a metal piston filled with a room temperature perfect gas at 1 atm of pressure. I expand the gas by pulling on the plunger. The gas of course initially cools, but then warms back to room temperature since it is in a non-insulating metal cylinder. **a.** What is the net ΔU? **(3 pts)**

b. While still pulling on the plunger after it warmed to room temperature, I wrap it in insulating glass wool to make the system adiabatic. I then suddenly stop pulling on it. As no heat can be exchanged with the outside, tell me if the piston will expand, compress, or stay the same. What are the reasons for your answer? **(3 pts)**

Chapter 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):

$$\mathrm{H} = \mathrm{U} + \mathrm{PV} \tag{3.1}$$

One simple description of enthalpy is that it accounts for the ability to do work as represented by the addition of PV in eq. 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:

$$\frac{\partial\big(\mathrm{f(x)} \cdot \mathrm{g(x)}\big)}{\partial \mathrm{x}} = \mathrm{f(x)}\frac{\partial \mathrm{g(x)}}{\partial \mathrm{x}} + \mathrm{g(x)}\frac{\partial \mathrm{f(x)}}{\partial \mathrm{x}} \tag{3.2}$$

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

$$\partial(\mathrm{f} \cdot \mathrm{g}) = \mathrm{f} \cdot \partial \mathrm{g} + \mathrm{g} \cdot \partial \mathrm{f} \tag{3.3}$$

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

$$\partial \mathrm{H} = \partial \mathrm{U} + \partial(\mathrm{P} \cdot \mathrm{V}) = \partial \mathrm{U} + \mathrm{V}\,\partial \mathrm{P} + \mathrm{P}\,\partial \mathrm{V} \tag{3.4}$$

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

$$\partial \mathrm{H} = \partial \mathrm{U} + \mathrm{P}\,\partial \mathrm{V} \tag{3.5}$$

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

$$\partial \mathrm{H} = \partial \mathrm{q} - \mathrm{P}\,\partial \mathrm{V} + \mathrm{P}\,\partial \mathrm{V} = \partial \mathrm{q}$$

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 eq. 3.4: $\partial \mathrm{H} = \partial \mathrm{U} + \partial(\mathrm{P} \cdot \mathrm{V})$. First, let's tackle isothermal transitions, both reversible and irreversible. Starting with $\partial \mathrm{U}$, we already learned that $\partial \mathrm{U} = 0\ \mathrm{J}$ 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: $\partial \mathrm{U} = \mathrm{C_V}\,\partial \mathrm{T}$, which is likewise $0\ \mathrm{J}$ under isothermal conditions ($\partial \mathrm{T} = 0\ \mathrm{K}$). The formula $\partial \mathrm{U} = \mathrm{C_V}\,\partial \mathrm{T}$ works for both isothermal and adiabatic transitions because $\partial \mathrm{U}$ is an exact differential, and as a result we can simplify our formula for changing enthalpy: $\partial \mathrm{H} = \mathrm{C_V}\,\partial \mathrm{T} + \partial(\mathrm{P} \cdot \mathrm{V})$. Next, we must figure out what to do with the $\partial(\mathrm{P}\cdot\mathrm{V})$ 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:

$$\partial(\mathrm{P}\cdot\mathrm{V}) = \mathrm{nR}\,\partial\mathrm{T} \tag{3.6}$$

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

$$\partial\mathrm{H} = \mathrm{C_V}\,\partial\mathrm{T} + \mathrm{nR}\,\partial\mathrm{T} = (\mathrm{C_V} + \mathrm{nR})\,\partial\mathrm{T} \tag{3.7}$$

We will use eq. 3.6 for many problems, and as it applies here it shows that $\partial\mathrm{H} = 0\ \mathrm{J}$ 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 $\Delta\mathrm{T}$ from eq. 2.14 (reversible) or eq. 2.15 (irreversible) and use that result into the integrated form of eq. 3.7: $\Delta\mathrm{H} = (\mathrm{C_V} + \mathrm{nR})\Delta\mathrm{T}$. This will also apply to both reversible and irreversible adiabatic transitions since $\partial\mathrm{H}$ is exact. As we pointed out in Ch. 2 that $\mathrm{C_P} = \mathrm{C_V} + \mathrm{nR}$, which we will prove rigorously below, it is also true that $\Delta\mathrm{H} = \mathrm{C_P}\Delta\mathrm{T}$

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. $\partial\mathrm{q} = 0\ \mathrm{J}$)? 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:

$$\partial\mathrm{U} = \partial\mathrm{w} + \partial\mathrm{q} = -\mathrm{P}\,\partial\mathrm{V}$$

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

$$\left.\frac{\partial\mathrm{U}}{\partial\mathrm{V}}\right)_{\mathrm{q}} = -\mathrm{P}\left.\frac{\partial\mathrm{V}}{\partial\mathrm{V}}\right)_{\mathrm{q}} = -\mathrm{P}$$

where we used the fact that $\left.\frac{\partial\mathrm{V}}{\partial\mathrm{V}}\right)_{\mathrm{q}} = 1$. As pressure is always positive, $-\mathrm{P}$ 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. $\left.\frac{\partial\mathrm{U}}{\partial\mathrm{V}}\right)_{\mathbf{q}}$ and $\left.\frac{\partial\mathrm{V}}{\partial\mathrm{V}}\right)_{\mathbf{q}}$, thus, it isn't

Example Problems

Problem 3.1: Prove that $\left.\frac{\partial U}{\partial T}\right)_V > 0\ \mathrm{J/K}$ (i.e. is positive) under constant volume conditions.

Answer: Starting with $\partial U = \partial q + \partial w = \partial q - P\,\partial V$ where reversible work is used due to ∂U's exactness. Since we stipulate that $\partial q = C_V\,\partial T$ and $P\,\partial V = 0$ J at constant volume ($\partial V = 0\ \mathrm{m^3}$): $\partial U = C_V\,\partial T$ and thus: $\left.\frac{\partial U}{\partial T}\right)_V = C_V\left.\frac{\partial T}{\partial T}\right)_V = C_V > 0\ \mathrm{J/K}$ since C_V is always positive.

Problem 3.2: Find the relationship between $\left.\frac{\partial U}{\partial T}\right)_P$ and C_P. You should assume perfect gas behavior.

Answer: At constant pressure $\partial q = C_P\,\partial T$, and thus: $\partial U = C_P\,\partial T - P\,\partial V$. Division by ∂T at constant pressure gives:

$$\left.\frac{\partial U}{\partial T}\right)_P = C_P\left.\frac{\partial T}{\partial T}\right)_P - P\left.\frac{\partial V}{\partial T}\right)_P = C_P - nR$$

where we used the fact that $-P\left.\frac{\partial V}{\partial T}\right)_P = -P\frac{nR}{P} = -nR$.

Problem 3.3: Is $C_P - nR$ positive or negative?

Answer: In our discussion on heat capacity, we stated that $C_{P,m}$ is always greater than R; in fact the smallest is can be is $\frac{5}{2}R$ for a monotonic gas. As a result, if $C_{P,m} - R > 0$ J/mol, then it must be true that $C_P - nR > 0\ J$. Thus, internal energy increases with increasing temperature under constant pressure conditions. In fact, if we rearrange the above as: $C_P = \left.\frac{\partial U}{\partial T}\right)_P + nR$, this appears to be very similar to our previous derivation that: $C_P = C_V + nR$. This makes us believe that $\left.\frac{\partial U}{\partial T}\right)_P = C_V$. Is this a fact? Read on to the next section to see the answer!

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 ever 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 $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{q}}$ is negative! Example problem 3.1 is provided to give you some more practice with proofs.

You may have noticed that work, $\partial \mathrm{w} = -\mathrm{P}_{\mathrm{ext}}\,\partial \mathrm{V}$, is always assumed to be reversible: $\partial \mathrm{w} = -\mathrm{P}\,\partial \mathrm{V}$ in just about anything we do when it comes to calculating or deriving $\partial \mathrm{U}$ or $\partial \mathrm{H}$. 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 for these derivations, which makes the effort significantly simpler. We don't have to use reversible work since we would still determine the same $\partial \mathrm{U}$ or $\partial \mathrm{H}$; however, it isn't sensible to intentionally make these determinations more complex.

3.2 Heat Capacities. At this point we have developed enough thermodynamic variables to derive more complex relationships. For example, we have shown that $\partial \mathrm{H} = \partial \mathrm{q}$ at constant pressure. Since $\partial \mathrm{q} = \mathrm{C_P}\,\partial \mathrm{T}$ at constant P, then $\partial \mathrm{H} = \mathrm{C_P}\,\partial \mathrm{T}$ which allows us to define heat capacity at constant pressure as $\mathrm{C_P} = \left.\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$. We also need to reconcile this with the fact that we previously derived: $\partial \mathrm{H} = (\mathrm{C_V} + \mathrm{nR})\,\partial \mathrm{T}$, which is consistent with our observation in Chapter 2 that: $\mathrm{C_P} = \mathrm{C_V} + \mathrm{nR}$. We will derive an exact proof of this relationship between the two forms of heat capacity. In fact, there are two derivational routes to do so, and we will show both. It is also instructive to see that there are multiple methods to demonstrate thermodynamic relationships.

Method 1: We have already shown that $\partial \mathrm{U} = \partial \mathrm{w} + \partial \mathrm{q} = -\mathrm{P}\,\partial \mathrm{V} + \partial \mathrm{q}$. If we bring $\partial \mathrm{q}$ to the left side of the equation:

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

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

$$\left.\frac{\partial \mathrm{q}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{C_P} = \mathrm{C_V}\left.\frac{\partial \mathrm{T}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \mathrm{P}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

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

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

$$\partial \mathrm{H} = \partial \mathrm{U} + \partial(\mathrm{PV}) = \partial \mathrm{U} + \mathrm{V}\,\partial \mathrm{P} + \mathrm{P}\,\partial \mathrm{V}$$

we divide by $\partial \mathrm{T}$:

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

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:

$$\left.\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \mathrm{V}\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \mathrm{P}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

Since $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{C_P}$ by definition and $\mathrm{V}\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = 0\ \mathrm{m^3Pa/K}$ since $\partial \mathrm{P} = 0$ Pa at constant pressure:

$$\mathrm{C_P} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \mathrm{P}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

Last, $\mathrm{P}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{P}\left.\frac{\partial \mathrm{nRT}/\mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{P}\frac{\mathrm{nR}}{\mathrm{P}} = \mathrm{nR}$ using the perfect gas law, so we now see that:

$$\mathrm{C_P} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \mathrm{nR}$$

We are so close to proving $\mathrm{C_P} = \mathrm{C_V} + \mathrm{nR}$, but we can't just state $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \mathrm{C_V}$ arbitrarily. But it must be true that $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}}$! Let's show this with another proof by deriving $\partial \mathrm{U}$ with changing T and V:

$$\partial \mathrm{U} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \partial \mathrm{T} + \left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \partial \mathrm{V}$$

(recall that this is the proper form for the change in a multivariable function from pg. 30). Next, we can divide by $\partial \mathrm{T}$:

$$\frac{\partial \mathrm{U}}{\partial \mathrm{T}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \frac{\partial \mathrm{T}}{\partial \mathrm{T}} + \left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \frac{\partial \mathrm{V}}{\partial \mathrm{T}}$$

We haven't set a variable constant, and for the purposes of this proof, we will set pressure constant:

$$\left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \left.\frac{\partial \mathrm{T}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$$

And now we can make several simplifications. For one, $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = 1$, $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \mathrm{C_V}$ (by definition), and $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = 0\ \mathrm{J/K}$ because $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = 0\ \mathrm{J/m^3}$. Why is that? Because we can infer $\partial \mathrm{U} = 0$ 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: $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \mathrm{C_V}$, and going back to: $\mathrm{C_P} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{T}}\right)_{\mathrm{P}} + \mathrm{nR}$, we can finally finish the proof:

$$\mathrm{C_P} = \mathrm{C_V} + \mathrm{nR} \tag{3.8}$$

To summarize, we have defined a new type of energy, called enthalpy, via $\mathrm{H = U + PV}$. 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 $\partial\mathrm{U} = \partial\mathrm{q}$ and $\partial\mathrm{H} = \partial\mathrm{q}$ at constant V and P, respectively. This can be understood using 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 $\partial\mathrm{U} = \partial\mathrm{w} = -\mathrm{P}\,\partial\mathrm{V}$. This makes internal energy U connected to 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 $\partial\mathrm{U} = \partial\mathrm{q}$.

Now we need to formalize some relationships using calculus. Recall that the change of a function f(x) is:

$$\partial\mathrm{f(x)} = \frac{\partial\mathrm{f}}{\partial\mathrm{x}}\partial\mathrm{x}$$

When applied to thermodynamic functions, we say that x is the natural variable of function f, and $\frac{\partial\mathrm{f}}{\partial\mathrm{x}}$ is the conjugate of x. Let's take the function f and transform it to a function g through the following:

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

What are the natural variables of g? To find out, we must determine $\partial\mathrm{g}$ and see what makes it change:

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

Thus $\partial\mathrm{g} = -\mathrm{x}\cdot\partial\left(\frac{\partial\mathrm{f}}{\partial\mathrm{x}}\right)$, and one can correctly conclude that $\left(\frac{\partial\mathrm{f}}{\partial\mathrm{x}}\right)$ is a natural variable of function g. You might be asking how can the derivative $\left(\frac{\partial\mathrm{f}}{\partial\mathrm{x}}\right)$ also be variable? Is it meaningful to ask what is the change of a derivative? To address this, let's examine the change in a function like internal energy under adiabatic, reversible conditions: $\partial \mathrm{U} = -\mathrm{P}\,\partial \mathrm{V}$. Given the definition of a function's differential: $\partial \mathrm{f}(\mathrm{x}) = \frac{\partial \mathrm{f}}{\partial \mathrm{x}} \partial \mathrm{x}$, if we substitute $\mathrm{U} = \mathrm{f}(\mathrm{x})$ and $\mathrm{V} = \mathrm{x}$, then we can also see that: $\partial \mathrm{U} = \frac{\partial \mathrm{U}}{\partial \mathrm{V}} \partial \mathrm{V} = -\mathrm{P}\,\partial \mathrm{V}$ which means $\frac{\partial \mathrm{f}}{\partial \mathrm{x}} = \frac{\partial \mathrm{U}}{\partial \mathrm{V}} = -\mathrm{P}$. Thus, negative pressure is conjugate to the natural variable volume.

Now let's repeat the transformation above:

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

where $\mathrm{f}(\mathrm{x}) = \mathrm{U}$, $\mathrm{x} = \mathrm{V}$, and $\frac{\partial \mathrm{f}}{\partial \mathrm{x}} = -\mathrm{P}$:

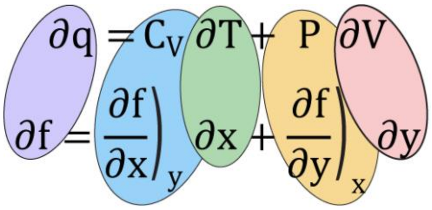
$$\mathrm{U} - \left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right) \cdot \mathrm{V} = \mathrm{U} - (-\mathrm{PV}) = \mathrm{U} + \mathrm{PV}$$

which we will call the enthalpy, mostly because, this is the equation for enthalpy. To determine enthalpy's natural variables, we will derive its differential:

$$\partial \mathrm{H} = \partial \mathrm{U} + \partial(\mathrm{PV}) = -\mathrm{P}\,\partial \mathrm{V} + \mathrm{P}\,\partial \mathrm{V} + \mathrm{V}\,\partial \mathrm{P} = \mathrm{V}\,\partial \mathrm{P}$$

Hence pressure is a natural variable of H, and $\frac{\partial \mathrm{H}}{\partial \mathrm{P}} = \mathrm{V}$ is conjugate to pressure. Although we have performed this derivation by invoking adiabatic reversible conditions, it is true that $\mathrm{H} = \mathrm{U} + \mathrm{PV}$ for any transition since U and H are state variables. The process of taking a function and subtracting its natural variable times the natural variable's conjugate is called a Legendre transform.

3.3.1 Inexactness of q. At this point, all this talk of natural variables and conjugates may be overwhelming and too abstract. We will slow down and work an example to help solidify your understanding. To this end, recall in Chapter 2 we were easily able to demonstrate $\partial \mathrm{w}$ is inexact due to the fac that reversible and irreversible work are not the same. With all this heat capacity and practice with partials we can now demonstrate that $\partial \mathrm{q}$ is inexact. First, we start with the familiar relation: $\partial \mathrm{U} = \partial \mathrm{q} + \partial \mathrm{w}$ and therefore $\partial \mathrm{q} = \partial \mathrm{U} - \partial \mathrm{w} = \partial \mathrm{U} + \mathrm{P}\,\partial \mathrm{V}$ if we follow the reversible path. Now we need to express the change in U with temperature at constant volume, which is the role of the heat capacity: $\partial \mathrm{U} = \mathrm{C_V}\,\partial \mathrm{T}$. As a result, $\partial \mathrm{q} = \mathrm{C_V}\,\partial \mathrm{T} + \mathrm{P}\,\partial \mathrm{V}$. If we line this up with the expression for the change in a function: $\partial \mathrm{f}(\mathrm{x}, \mathrm{y}) = \left.\frac{\partial \mathrm{f}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \partial \mathrm{x} + \left.\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \partial \mathrm{y}$:



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 the Euler Test:

$$\left.\frac{\partial}{\partial y}\left.\frac{\partial f}{\partial x}\right)_y\right)_x \neq \left.\frac{\partial}{\partial x}\left.\frac{\partial f}{\partial y}\right)_x\right)_y$$

Making the proper substitutions yields:

$$\left.\frac{\partial}{\partial V}\left.\frac{\partial q}{\partial T}\right)_V\right)_T \neq \left.\frac{\partial}{\partial T}\left.\frac{\partial q}{\partial V}\right)_T\right)_V$$

The right-hand derivative term is: $\left.\frac{\partial}{\partial T}\left.\frac{\partial q}{\partial V}\right)_T\right)_V = \left.\frac{\partial P}{\partial T}\right)_V$. We assume perfect gas conditions, i.e. $P = \frac{nRT}{V}$, leaving us with: $\left.\frac{\partial}{\partial T}\left.\frac{\partial q}{\partial V}\right)_T\right)_V = \left.\frac{\partial P}{\partial T}\right)_V = \frac{\partial nRT/V}{\partial T} = \frac{nR}{V}$.

The left-hand side is: $\left.\frac{\partial}{\partial V}\left.\frac{\partial q}{\partial T}\right)_V\right)_T = \left.\frac{\partial C_V}{\partial V}\right)_T$ since $\partial q = C_V\,\partial T$. Unfortunately, $\left.\frac{\partial C_V}{\partial V}\right)_T$ is a bit complicated to evaluate. Recall that the heat capacity at constant volume is related to the internal energy via: $C_V = \left.\frac{\partial U}{\partial T}\right)_V = \frac{1}{2}nR \cdot (\text{degrees of freedom})$ as we demonstrated in Sec. 2.5 of Chapter 2. 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 $\left.\frac{\partial C_V}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$. Thus, heat is not exact because it fails the Euler test as:

$$\left.\frac{\partial}{\partial V}\left.\frac{\partial q}{\partial T}\right)_V\right)_T = \mathbf{0\ J/m^3} \neq \frac{\mathbf{nR}}{\mathbf{V}} = \left.\frac{\partial}{\partial T}\left.\frac{\partial q}{\partial V}\right)_T\right)_V$$

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 this does work, sometimes using

The Euler Chain

The Euler Chain formula is a useful mathematical tool and will be used throughout this text. As such, we want to show you how it is derived. Starting with the change in x and a function of y and z:

$$\partial x = \left.\frac{\partial x}{\partial y}\right)_z \partial y + \left.\frac{\partial x}{\partial z}\right)_y \partial z$$

Now divide by ∂y:

$$\frac{\partial x}{\partial y} = \left.\frac{\partial x}{\partial y}\right)_z \frac{\partial y}{\partial y} + \left.\frac{\partial x}{\partial z}\right)_y \frac{\partial z}{\partial y}$$

As stated previously, we can now choose what to hold constant. To do this derivation in the shortest number of steps we hold x constant: $\left.\frac{\partial x}{\partial y}\right)_x = \left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial y}\right)_x + \left.\frac{\partial x}{\partial z}\right)_y \left.\frac{\partial z}{\partial y}\right)_x$. Now we can simplify several terms because $\left.\frac{\partial x}{\partial y}\right)_x = 0$ and $\left.\frac{\partial y}{\partial y}\right)_x = 1$. Thus: $0 = \left.\frac{\partial x}{\partial y}\right)_z + \left.\frac{\partial x}{\partial z}\right)_y \left.\frac{\partial z}{\partial y}\right)_x$ which simplifies to the Euler Chain formula:

$$\left.\frac{\partial x}{\partial y}\right)_z = -\left.\frac{\partial x}{\partial z}\right)_y \left.\frac{\partial z}{\partial y}\right)_x \tag{3.9}$$

Often this appears in a different form; dividing the right by the left side:

$$\frac{\left.\frac{\partial x}{\partial y}\right)_z}{\left.\frac{\partial z}{\partial y}\right)_x \left.\frac{\partial x}{\partial z}\right)_y} = \left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$$

This is how the Euler Chain formula is more typically expressed.

contraptions nearly the size of a house. Ultimately, Joule's ability to demonstrate that work energy can transform into heat energy lead to the 1st Law of Thermodynamics.

Part of Joule's research centered on evaluating whether any of the thermodynamics they knew really made sense, especially concerning work and heat. For example- 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 when "adiabatic" is written). Inside of this device is a pressurized container with that will expand into another that is evacuated; this is shown in Figure 3.1. If the gas cools, 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.

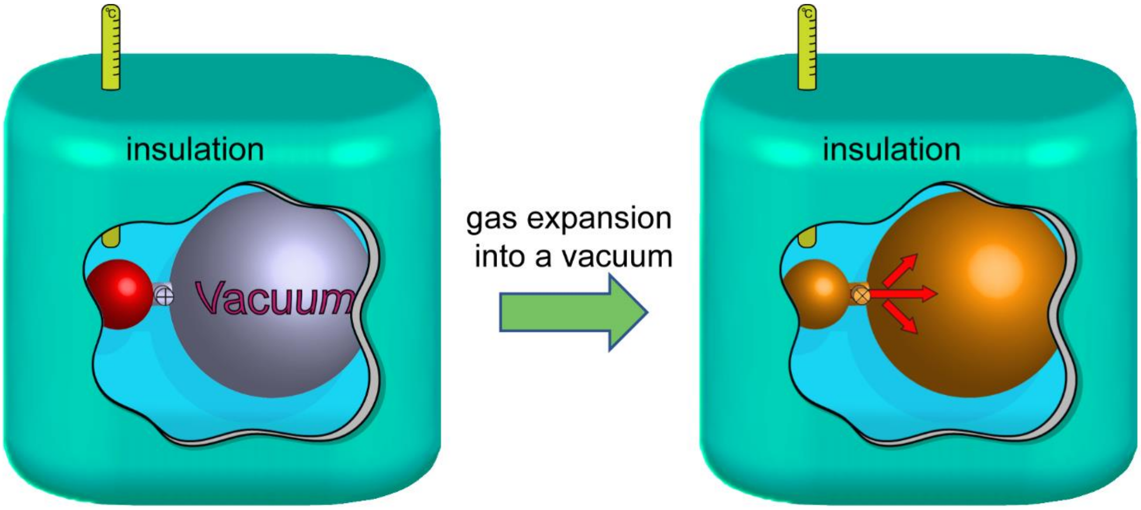


Figure 3.1. The Joule experiment is an iso-internal energy system in which a gas expands inside an insulated water bath. A change in temperature is due to real gas behavior.

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. Actually, if you use hydrogen or helium, the water gets slightly hotter. It seems that this system is much more complicated than originally though. To delve deeper, we need to determine $\left.\frac{\partial T}{\partial V}\right)_{?}$, but it isn't clear what variable is held constant. 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, eq. 3.8, 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:

$$\mu_J = \left.\frac{\partial T}{\partial V}\right)_{U} = -\frac{1}{C_V}\cdot\left.\frac{\partial U}{\partial V}\right)_{T} \tag{3.10}$$

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 either as $\partial U = C_V\,\partial T$. The Joule coefficient (μ_J) likewise should be ~0 K/m^3 since it is equal to $\left.\frac{\partial T}{\partial V}\right)_U$, and we just showed that we expect $\partial T =$ 0 K. But then again, the measured change in temperature was only *close* to 0 K, not *exactly* zero. This behavior can be understood when we view the Joule coefficient as $\mu_J = -\frac{1}{C_V}\cdot\left.\frac{\partial U}{\partial V}\right)_T$. As you will see at the end of Chapter 4, you will be able to prove that $\left.\frac{\partial U}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$ for a perfect gas, but $\left.\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ for a van der Waals gas. We know already that a (real) van der Waals gas differ from a perfect gas because real gas molecules interact, which must affect their internal energy. Most gas molecules have energy-lowering self-interactions via the "a" parameter as explained in Chapter 1, which means that getting closer as the volume decreases $(\partial V < 0\ \mathrm{m}^3)$ lowers the energy$(\partial U < 0\ \mathrm{J})$, 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. And hydrogen and helium have to be oddballs- they get hotter when expanded in a Joule apparatus.

3.4.1 The Joule-Thomson Experiment. Now 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 just like mass and is only transferred 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 their thermodynamics knowledge 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

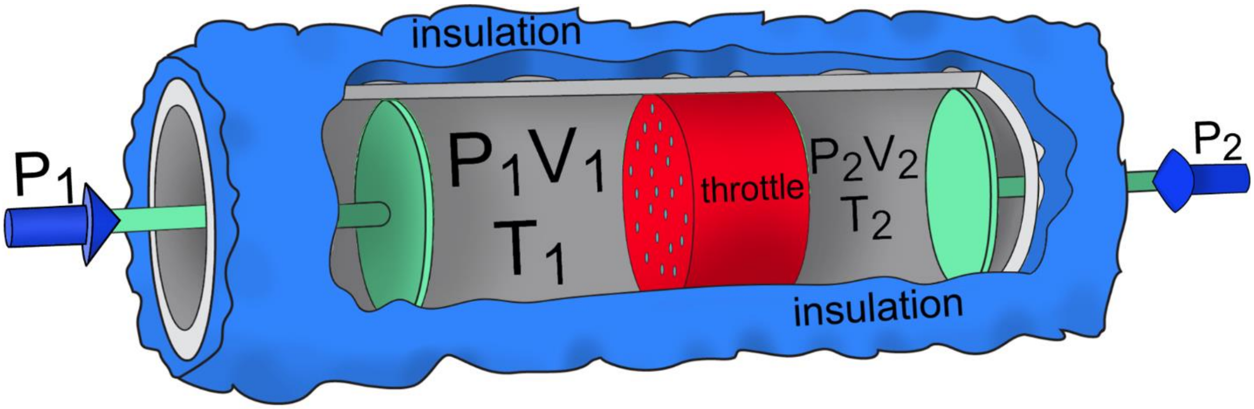


Figure 3.2. The Joule-Thomson device is an isoenthalpic system to perform constant pressure work on a gas. A temperature change demonstrates real gas behavior.

the gas ends up on the right side of the device in state 2, so the final internal energy is U_2; mathematically the change in internal energy is:

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

The system is adiabatic ($\partial q \ = 0$ J), which means that the change 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 1st vessel is constant as the plunger is compressed, resulting in:

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

Likewise, the work on the right side is:

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

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. As before we will begin with the Euler chain: $\left.\frac{\partial x}{\partial y}\right)_z = -\left.\frac{\partial x}{\partial z}\right)_y \left.\frac{\partial z}{\partial y}\right)_x$: and apply it to $\left.\frac{\partial T}{\partial P}\right)_H$, where $x = T$, $y = P$ and $z = H$ to determine the Joule-Thomson coefficient:

$$\mu_{J-T} = \left.\frac{\partial T}{\partial P}\right)_H = -\left.\frac{\partial T}{\partial H}\right)_P \left.\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P}\left.\frac{\partial H}{\partial P}\right)_T \qquad (3.11)$$

And as with Joule's experiment, there should be no temperature change because $\left.\frac{\partial H}{\partial P}\right)_T$ should be 0 J/Pa (there is no change in enthalpy for isothermal transitions). However, depressurizing a gas generally results in a modest cooling, which is due to real gas behavior. For various reasons, the cooling of a gas is much easier under isoenthaplic conditions, and the Joule-Thomson experiment lead to modern refrigeration. Shown in Table 3.0 are various Joule-Thomson coefficients, where we can see that most gases have positive coefficients which causes the gas cools upon depressurization. The effect is rather large for ammonium and Freon, and again we see that hydrogen is an outlier which indicates that real gas behavior is responsible for these effects. Because of ammonia's large positive μ_{J-T} the first refrigeration plants used ammonium as a coolant, which was as bad an idea as it sounds. People then used Freon, aka 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 a good idea. Or so we think; note that R410A is a powerful greenhouse gas.

Gas	μ_{J-T} (K atm^{-1})
Helium	-0.062
air	0.227
CO_2	1.11
Freon	1.20
NH_3	3.39

Table 3.0. Joule-Thomson coefficients for select gases.

As part of the Chapter 5 homework problems you will be able to demonstrate that $\left.\frac{\partial H}{\partial P}\right)_T = 0\ \mathrm{J/Pa}$ for a perfect gas, but $\left.\frac{\partial H}{\partial P}\right)_T \approx nb - \frac{2na}{RT}$ is for a real (van der Waals) gas. To do these derivations you have to know some things about entropy, which allows us to understand more about heat. This also gives you more tools to perform much more advanced thermodynamic derivations.

Conclusion. This chapter has shown you how the conditions of transformations require examination by a different set of equations for energy. This was done by demonstrating the differences between constant volume vs. constant pressure processes. At constant temperature. But what if temperature isn't constant? As we move forward, we will study changes in temperature further, but as you now realize that Legendre transformation requires us to know the conjugate variable of temperature. And that variable is entropy.

Problems: Numerical

1. Inside my perfect gas engine, 4.4 g at 25 °C of CO_2 gas expands from 0.5 L to 1.0 L reversibly and adiabatically. What is Δq, ΔV, ΔT, Δw, ΔU and ΔH for this process? ($C_{p,m}$ = 36.94 J/K/mol and $C_{v,m}$ = 28.46 J/K/mol for CO_2). Hint: ΔT= -54.65K, Δw= -156 J. **(10 pts)**

2. Let's say I have 0.5 mol xenon gas in a metal (non-expanding) 2 L box at 25 °C. If I put it over a candle and add 1.0 kJ of energy, the gas is heated up to 110 °C. Calculate Δq, Δw, ΔU, and ΔH for this process. Use the van der Waals equation to figure this out. **(10 pts)**

Hint: Once you figure out how to calculate Δ(P·V), you should find that ΔH is 1.36 kJ.

3. Let's say I have 951 mol N_2 gas in a 235.6 L turbine (constant volume) at 25 °C. If I burn enough fuel to add 11.36 MJ of energy, the gas will heat up to 600 °C. Calculate Δq, Δw, ΔU, ΔH, and $C_{V,m}$ for this process. Use the van der Waals equation to calculate ΔH!! **(10 pts)**

Hint: If it was a perfect gas ΔH would have been 15.9 MJ; your answer will be higher.

4. a. In question 3 above, calculate $C_{P,m}$ for nitrogen by ΔH/ΔT/n. **b.** However, if I Google the heat capacity, I see that at room temperature $C_{P,m}$ = 29.135 J/K/mol and the result from pt. a is slightly higher. As they are not exactly the same, can you explain the discrepancy? **(4 pts)**

5. Changes in the heat capacity at constant pressure with temperature can be modeled as:

$C_{P,m} = a + b \times T + \frac{c}{T^2}$. **a.** What are the units of a, b, and c? **(2 pts)**

b. For nitrogen gas, a = 28.58, b = 0.00377, c = -50,000. What is the heat capacity at 600 °C? **(2 pts)**

6. One can store energy by compressing air, and then later use it to power a turbine to create energy when needed. However, you have to heat the room temperature compressed air to make this effective. You can avoid this if you initially compress the air under adiabatic conditions, so the gas is already hot when you need it to generate electricity. This is called adiabatic compressed air energy storage (CAES). Inside a typical power plant, 5.8×10^6 kg of N_2 gas is at 25 °C is compressed from atmospheric to pressure into a volume of 300,000 m^3 (they use abandoned salt mines). The process is done reversibly and adiabatically. What is Δq, n, V_i, P_f, ΔT, ΔU, Δw, and ΔH and for this process? ($C_{p,m}$ = 29.12 J/K/mol and $C_{v,m}$ = 20.80 J/K/mol for N_2). Assume perfect gas behavior. (**16 pts**)

7. If you store ~2.7×10^{12} J of internal energy as compressed air in a cave, and need to generate 1 GWatt of power (a Watt is J/second), how long can you run before power is out? (**4 pts**)

8. A four cylinder 1.2 L car engine has individual cylinders (pistons) that hold a total of 0.3 L of fuel + air gas mixture. When the fuel + air gas mixture enters the piston at 1 atm pressure at a standard engine temperature of ~90 °C (again 0.3 L volume), it is compressed adiabatically and irreversibly by a constant external pressure of 608 kPa. Assuming the $C_{v,m}$ of the fuel + air gas mixture is $C_{v,m}$ = 20.8 J/K/mol, what is Δq, n, P_f, T_f, ΔU, Δw, and ΔH? Assume perfect gas behavior. **(14 pts)**

9. Say 0.0101 moles of gas in a car engine cylinder under a pressure of 608 kPa at 882 K expands adiabatically and irreversibly against 1 atm pressure. The $C_{v,m}$ of the gas is 20.8 J/K/mol while $C_{p,m}$ = 29.12 J/K/mol, so what is Δq, V_i, T_f, P_f, ΔU, Δw, and ΔH? **(7 pts)**

10. Say 0.0101 moles of gas in a car engine cylinder at atmospheric pressure at 90 °C contracts adiabatically and reversibly until it is at 608 kPa pressure. The $C_{v,m}$ of the gas is 20.8 J/K/mol while $C_{p,m}$ = 29.12 J/K/mol, so what is Δq, T_f, ΔU, Δw, and ΔH? Hint: $\frac{P_i}{P_f} = \left(\frac{T_i}{T_f}\right)^{\frac{C_V+nR}{nR}}$ **(10 pts)**

11. Say 0.0101 moles of gas in a car engine cylinder under a pressure of 608 kPa at 606 K expands adiabatically and reversibly until it is at 1 atm pressure. The $C_{v,m}$ of the gas is 20.8 J/K/mol while $C_{p,m}$ = 29.12 J/K/mol, so what is Δq, T_f, ΔU, Δw, V_f, and ΔH? Hint: $\frac{P_i}{P_f} = \left(\frac{T_i}{T_f}\right)^{\frac{C_V+nR}{nR}}$ **(10 pts)**

Problems: Theoretical or Explain in Words

1. In questions 10 and 11 of the previous section, you may have noticed that the starting state in #11 was the end state in #10. Also the end state in #11 was the starting state in #10. Note that all the work, ΔU and ΔH were equal but opposite of each other. Now I can also tell you that in questions 8 and 9, you may have noticed that the starting state in #9 was the end state in #8. However, the end state in #9 was not the starting state in #8. Also, while the thermodynamic variables were of opposite sign, they were not equal in magnitude. Why is that happening? **(2 pts)**

2. According to the adiabatic equation of state: $\left(\frac{T_f}{T_i}\right)^{\frac{C_V}{nR}} = \frac{V_i}{V_f}$, expanding a gas will result in it getting cold. However, in the adiabatic Joule experiment, expanding a gas like hydrogen or helium will cause those gases to get hot (unlike all other gases). What gives? (**4 pts**)

3. Give a very simple reason why $\left.\frac{\partial U}{\partial V}\right)_T$ and $\left.\frac{\partial H}{\partial P}\right)_T$ are equal for a perfect gas? **(4 pts)**

4. Name *three* ways to measure how real gases differ from perfect gases. **(6 pts)**

5. The internal energy at constant temperature of a real gas is slightly affected by collisions; as there are more collisions in smaller volumes, the internal energy is affected more (U changes with V even at a constant temperature). For a perfect gas, the internal energy is not affected by changes in the volume at constant temperature. Why? **(2 pts)**

6. Does the fact that the Joule coefficient: $\mu_J = \left.\frac{-1}{C_V}\frac{\partial U}{\partial V}\right)_T$ has a small, finite value for real gases make the Equipartition Theorem wrong? **(2 pts)**

7. The text shows that: $\left.\frac{\partial U}{\partial T}\right)_V = \left.\frac{\partial U}{\partial T}\right)_P$. Can you show that: $\left.\frac{\partial H}{\partial T}\right)_V = \left.\frac{\partial H}{\partial T}\right)_P$? Hint, starting with: $\partial H = \left.\frac{\partial H}{\partial T}\right)_P \partial T + \cdots$

(**5 pts**)

8. a. Prove $\left.\frac{\partial T}{\partial V}\right)_U = -\left.\frac{\partial U}{\partial V}\right)_T \left.\frac{\partial U}{\partial T}\right)_V = \left.\frac{-1}{C_V}\frac{\partial U}{\partial T}\right)_T$ starting with: $\partial U = \left.\frac{\partial U}{\partial V}\right)_T \partial V + \left.\frac{\partial U}{\partial T}\right)_V \partial T$. (**5 pts**)

b. The equation for the Joule coefficient μ_J is $\left.\frac{\partial T}{\partial V}\right)_U = \left.\frac{-1}{C_V}\frac{\partial U}{\partial T}\right)_T$ can most easily be solved using the Euler chain formula: $\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$. Please show this to be the case. Hint: start with $\left.\frac{\partial T}{\partial V}\right)_U$ **(5 pts)**

9. a. Prove $\left.\frac{\partial T}{\partial P}\right)_H = -\left.\frac{\partial T}{\partial H}\right)_P \left.\frac{\partial H}{\partial P}\right)_T = -\left.\frac{1}{C_P}\frac{\partial H}{\partial P}\right)_T$ starting with: $\partial H = \left.\frac{\partial H}{\partial T}\right)_P \partial T + \left.\frac{\partial H}{\partial P}\right)_T \partial P$. (**5 pts**)

b. The equation for the Joule-Thomson coefficient μ_{JT} is $\left.\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left.\frac{\partial H}{\partial P}\right)_T$ can most easily be solved using the Euler chain formula: $\left.\frac{\partial x}{\partial y}\right)_z \left.\frac{\partial y}{\partial z}\right)_x \left.\frac{\partial z}{\partial x}\right)_y = -1$. Please show this to be the case. Hint: start with $\left.\frac{\partial T}{\partial P}\right)_H$. **(5 pts)**

10. Starting with: $\left.\frac{\partial H}{\partial P}\right)_T = \left.\frac{\partial(U+PV)}{\partial P}\right)_T$, can you show that $\left.\frac{\partial U}{\partial P}\right)_T$ and $\left.\frac{\partial H}{\partial P}\right)_T$ are in fact equal? Hint: you will need to use the perfect gas law. **(7 pts)**

11. I once calculated that the difference between the Joule-Thomson and Joule coefficient for a nearly perfect gas is: $(\mu_J - \mu_{JT}) \approx \frac{1}{C_P}\left.\frac{\partial U}{\partial P}\right)_T - \frac{1}{C_V}\left.\frac{\partial U}{\partial V}\right)_T$.

a. For a truly perfect gas, what is the difference? (this is sort of a trick question) **(2 pts)**

b. Most molecules “like” each other- thus U goes down if gas molecules become closer together by pressurizing the system. Thus, can you explain why μ_{JT} is bigger than μ_J? **(5 pts)**

12. The approximate relationship $(\mu_J - \mu_{JT}) \approx \frac{1}{C_P}\left.\frac{\partial U}{\partial P}\right)_T - \frac{1}{C_V}\left.\frac{\partial U}{\partial V}\right)_T$ has a significant flaw. What is it? hint: remember how unit analysis is emphasized in this course. **(5 pts)**

Chapter 4: Entropy and the 2nd Law

This chapter introduces entropy, which is the most important thing in the Universe. You might be familiar with the concept of entropy as the "buildings fall down" principle; however as we show here you have to add in "nothing works perfectly" to fully described the 2nd Law of Thermodynamics. This probably explains all the events of your life, which indeed do follow the basic tenet of increasing entropy. If you develop a method for measuring entropy, then you now have the 3rd Law of Thermodynamics as well.

4.1. Introduction to Entropy. There are several ways to describe entropy. For example, you may have heard on the street 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- entropy is how well heat diffuses through a system resulting in a temperature change, like how the solubility constant for a salt in water dictates the salinity. These descriptions are consistent with a change of entropy defined as:

$$\partial S = \frac{\partial \mathrm{q}}{\mathrm{T}} \tag{4.1}$$

(or $\Delta S = \frac{\Delta \mathrm{q}}{\mathrm{T}}$ if integrated). To make sure this makes sense let's apply it to situations that create "randomness" at a constant temperature, specifically phase changes. In this regard, boiling water generates more entropy than melting ice; as a result, it must be true that: $\frac{\Delta \mathrm{q_{vap}}}{\mathrm{T_{vap}}} \gg \frac{\Delta \mathrm{q_{melt}}}{\mathrm{T_{melt}}}$ if $\Delta S = \frac{\Delta \mathrm{q}}{\mathrm{T}}$ is correct. Water vaporization requires a lot of heat ($\Delta \mathrm{q_{vap}}$ = +41.7 kJ/mol) at a moderately high temperature ($\mathrm{T_{vap}}$ = 373 K). Melting ice occurs at a lower temperature ($\mathrm{T_{melt}}$ = 273 K) but doesn't require nearly as much heat ($\Delta \mathrm{q_{melt}}$ = +6.0 kJ/mol). Consequently:

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

Thus, the definition $\partial S = \frac{\partial \mathrm{q}}{\mathrm{T}}$ makes sense.

As further proof of this definition, we contend that the entropy of vaporization: $\Delta_{\mathrm{vap}}\mathrm{S} = \mathrm{S_{gas,m}} - \mathrm{S_{liq,m}}$, ought to be nearly the same for most chemical substances. This is because gases have very similar behavior as revealed by the near-universality of the perfect gas law that works regardless of the gas's chemical identity. Gases also have very high entropy while liquids have significantly less. As a result, the difference between the two ($\Delta_{\mathrm{vap}}\mathrm{S}$) isn't expected to vary much. Shown in Figure 4.1 is the enthalpy of vaporization, which is the heat exchange (Δq_{vap}) necessary to boil a substance at constant pressure, versus the boiling (vaporization) temperature T_{vap}. 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 as much is seen in Figure 4.1, 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 ~10.5 R, which is known as Trouton's Rule.

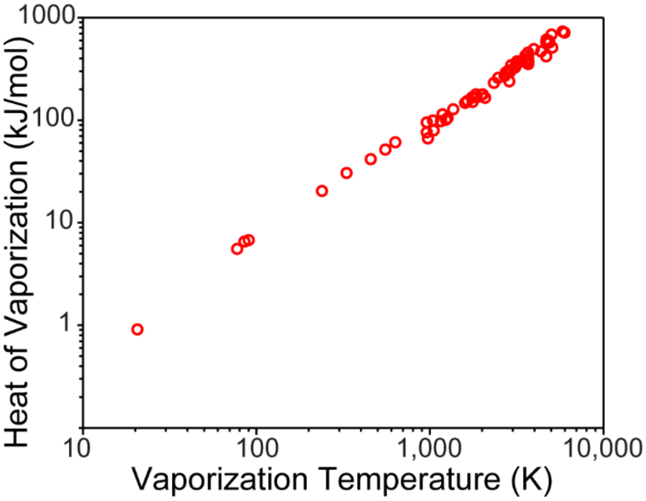


Figure 4.1. A plot of $\Delta_{vap}H$ vs boiling temperature reveals that the entropy of vaporization of many chemicals are similar in magnitude.

Entropy should be a state function, and if so $\frac{\partial q}{T}$ must be an exact partial differential. However, we previously demonstrated that ∂q is not exact and has path dependence, and it seems that $\frac{\partial q}{T}$ might likewise be inexact. Let's see if it is; starting with $\partial U = \partial q + \partial w$, we will first assume a reversible path ($\partial w = -P\,\partial V$) because ∂U is exact and insert $C_V\,\partial T$ for ∂U. Some rearrangement leaves us with:

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

Dividing by T yields:

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

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

$$\begin{aligned}\frac{\partial q}{T} &= \frac{C_V}{T}\partial T + \frac{P}{T}\partial V \\ \partial f &= \left.\frac{\partial f}{\partial x}\right)_y \partial x + \left.\frac{\partial f}{\partial y}\right)_x \partial y\end{aligned}$$

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

Exactness using the Euler test means:

$$\frac{\partial}{\partial y}\left.\left.\frac{\partial f}{\partial x}\right)_{y}\right)_{x} = \frac{\partial}{\partial x}\left.\left.\frac{\partial f}{\partial y}\right)_{x}\right)_{y}$$

when applied to $\frac{\partial q}{T}$:

$$\frac{\partial}{\partial V}\left.\left.\frac{\frac{\partial q}{T}}{\partial T}\right)_{V}\right)_{T} = \frac{\partial}{\partial T}\left.\left.\frac{\frac{\partial q}{T}}{\partial V}\right)_{T}\right)_{V}$$

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

The left-hand side: $\frac{\partial}{\partial V}\left.\left.\frac{\partial q/T}{\partial T}\right)_{V}\right)_{T}$ requires more examination. We are going to work this derivation in a slightly more complex fashion this time by ignoring the fact that $\left.\frac{\partial q/T}{\partial T}\right)_{V} = \frac{C_V}{T}$, and instead note that $\frac{\partial U}{T} = \frac{\partial q}{T}$ at constant volume because no work is done. This makes the left side: $\frac{\partial}{\partial V}\left.\left.\frac{\partial q/T}{\partial T}\right)_{V}\right)_{T} = \frac{\partial}{\partial V}\left.\left.\frac{\partial U/T}{\partial T}\right)_{V}\right)_{T}$ and since U is exact:

$$\frac{\partial}{\partial V}\left.\left.\frac{\partial U/T}{\partial T}\right)_{V}\right)_{T} = \frac{\partial}{\partial T}\left.\left.\frac{\partial U/T}{\partial V}\right)_{T}\right)_{V}$$

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

$$\frac{\partial}{\partial V}\left.\left.\frac{\partial q/T}{\partial T}\right)_{V}\right)_{T} = \frac{\partial}{\partial V}\left.0\right)_{T} = 0\ \mathrm{J/K^2/m^3}$$

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:

$$\frac{\partial}{\partial \mathrm{V}}\left.\left.\frac{\frac{\partial \mathrm{q}}{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{V}}\right)_{\mathrm{T}} = 0\,\frac{\mathrm{J}}{\mathrm{K}^2\mathrm{m}^3} = 0\,\frac{\mathrm{Pa}}{\mathrm{K}^2} = \frac{\partial}{\partial \mathrm{T}}\left.\left.\frac{\frac{\partial \mathrm{q}}{\mathrm{T}}}{\partial \mathrm{V}}\right)_{\mathrm{T}}\right)_{\mathrm{V}}$$

Now that we are done making our eyes bleed due to the calculus, if it is acceptable that $\frac{\partial \mathrm{q}}{\mathrm{T}}$ is exact then we can accept that $\partial \mathrm{S} = \frac{\partial \mathrm{q}}{\mathrm{T}}$ and $\partial \mathrm{q} = \mathrm{T}\,\partial \mathrm{S}$. However, we had to use the reversible path when applying the Euler test to $\frac{\partial \mathrm{q}}{\mathrm{T}}$, and thus $\partial \mathrm{S} = \frac{\partial \mathrm{q}_{\mathrm{rev}}}{\mathrm{T}}$. This makes the change in entropy path independent, which must be the case if $\partial \mathrm{S}$ is exact.

Before we go further in our analysis of $\partial \mathrm{S}$, the fact that $\partial \mathrm{q}_{\mathrm{rev}} = \mathrm{T}\,\partial \mathrm{S}$ offers up several opportunities for analysis that have been ignored thus far. For example:

$$\boldsymbol{\partial}\mathbf{U} = \partial \mathrm{q} + \partial \mathrm{w} = \mathbf{T}\boldsymbol{\partial}\mathbf{S} - \mathbf{P}\boldsymbol{\partial}\mathbf{V} \tag{4.2}$$

This is the change in internal energy as calculated reversibly. However, as internal energy is a state function, changes in U can be calculated reversibly even for transitions that are irreversible! Thus, the above relationship for $\partial \mathrm{U}$ is true no matter what. Likewise:

$$\boldsymbol{\partial}\mathbf{H} = \partial \mathrm{U} + \partial(\mathrm{PV}) = \mathrm{T}\,\partial \mathrm{S} - \mathrm{P}\,\partial \mathrm{V} + \mathrm{P}\,\partial \mathrm{V} + \mathrm{V}\,\partial \mathrm{P} = \mathbf{T}\boldsymbol{\partial}\mathbf{S} + \mathbf{V}\boldsymbol{\partial}\mathbf{P} \tag{4.3}$$

which is the same as derived before except $\mathrm{T}\,\partial \mathrm{S}$ replaces $\partial \mathrm{q}$. These 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. Consequently, if the system gains $\partial \mathrm{q}$ of heat, then the exterior must have lost $\partial \mathrm{q}$ of heat, perhaps more. And if so, both the system and surroundings have lost / gained entropy. This is important because the sum of the two is the total change of entropy; in fact why don't we call it the entropy change of the Universe. This is important because the 2nd Law of Thermodynamics states:

The entropy of the Universe is always increasing.

Therefore, it is important to thermodynamics to consider entropy changes in the system plus exterior to the system. Before we discuss this further, it must be stated that the very narrow definition: $\Delta S = \frac{\partial \mathrm{q}_{\mathrm{rev}}}{\mathrm{T}}$ is deficient. To illustrate, if the system gains $\frac{\partial \mathrm{q}_{\mathrm{rev}}}{\mathrm{T}}$ amount of entropy from the surroundings, then the surroundings must have lost $\frac{-\,\partial \mathrm{q}_{\mathrm{rev}}}{\mathrm{T}}$ worth of entropy. As a result, it appears that the total change in entropy for any process is: $\Delta S_{tot} = \frac{\partial q_{rev}}{T} - \frac{\partial q_{rev}}{T} = 0$ J/K. This is not the case; for example, imagine heating a system composed of a can, where the heat generated by the exterior is from a candle placed underneath it as in Figure 2.0. There is heat from the exterior added to the system, which increases the entropy of the system as calculated by $\frac{\partial q_{rev}}{T}$. But the setup is very inefficiency, and a lot of heat is dissipated by the exterior into the exterior. By the fact that the exterior must be slightly warmer as a result, then the change in the entropy of the outside is $> \frac{-\partial q_{rev}}{T}$. This assures that the sum of the interior and exterior entropy is >0 J/K. We need to delineate 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. The discussion below defines how an efficient exchange of thermal energy is reversible, whereas a “lossy” (or inefficient) energy exchange is irreversible. Consider an isothermal process, which means that $\partial U = \partial q + \partial w = 0$ J because of the Equipartition theorem. Thus $\partial q = -\partial w$, which is a manifestation of the 1st Law. In Section 2.2 we demonstrated graphically how reversible work must always be the most negative. Mathematically, this is equivalent to: $\partial w_{irrev} > \partial w_{rev}$. To cast a wider net, we can restate this in a more generic fashion as: $\partial w \geq \partial w_{rev}$, where we don’t specify whether ∂w is reverisible or irreversible. The equivalence exists in the case of the process being reversible.

Now back to the isothermal process where $\partial q = -\partial w$, and thus for anything true of work the reverse is true of heat. Consequently, if: $\partial w \geq \partial w_{rev}$, then:

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

If we divide both sides of the above by T: $\frac{\partial q_{rev}}{T} \geq \frac{\partial q}{T}$, we see that:

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

due to the definition of the change in system entropy as $\frac{\partial q_{rev}}{T}$. If we subtract $\frac{\partial q}{T}$ from both sides:

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

and note that we have not stated whether ∂q of the process is reversible or irreversible. 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 $\partial \mathrm{S}_{\mathrm{exterior}} = \frac{-\partial \mathrm{q}}{\mathrm{T}}$. Now let's revise the statement $\partial \mathrm{S} - \frac{\partial \mathrm{q}}{\mathrm{T}} \geq 0\ \mathrm{J/K}$ as:

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

which also means that:

$$\partial \mathrm{S}_{\mathrm{total}} \geq 0\ \mathrm{J/K} \tag{4.4}$$

given that $\partial \mathrm{S}_{\mathrm{total}} = \partial \mathrm{S} + \partial \mathrm{S}_{\mathrm{exterior}}$. It seems that we have proven the 2nd Law! In fact, we state that any process for which the total entropy increases is a "spontaneous" process, which is a fancy way of saying that "it happens". Spontaneous processes include buildings falling down and forest fires in California. 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 2nd Law means $\partial \mathrm{S}_{\mathrm{total}} \geq 0\ \mathrm{J/K}$, where the equality sign applies to systems at equilibrium.

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

$$\partial \mathrm{q} - \mathrm{T}\,\partial \mathrm{S} \leq 0\ \mathrm{J}$$

(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: $\partial \mathrm{U} = \partial \mathrm{q} + \partial \mathrm{w}$, and no work can be done at constant volume, then $\partial \mathrm{U} = \partial \mathrm{q}$. Now we are left with:

$$\partial \mathrm{U} - \mathrm{T}\,\partial \mathrm{S} \leq 0\ \mathrm{J}$$

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 ($\partial \mathrm{S} = 0\ \mathrm{J/K}$). Now:

$$\partial \mathrm{U} \leq 0\ \mathrm{J}$$

At this point we can make a "big picture" statement. Recall that the derivation of the above began with: $\partial \mathrm{S}_{\mathrm{total}} \geq 0\ \mathrm{J/K}$, which again means that the total entropy of a spontaneous process increases. At the end of the derivation, $\partial \mathrm{U} \leq 0\ \mathrm{J}$, we demonstrated that internal energy must decrease or stay the same. 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: $\partial \mathrm{q} - \mathrm{T}\,\partial \mathrm{S} \leq 0\ \mathrm{J}$. What if we were examining a constant pressure system instead? In that case, as we showed in Sec. 3.1: $\partial \mathrm{H} = \partial \mathrm{q}$. Now we have:

$$\partial \mathrm{H} - \mathrm{T}\,\partial \mathrm{S} \leq 0\ \mathrm{J}$$

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

$$\partial \mathrm{H} \leq 0\ \mathrm{J}$$

Let's restate this- 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 $\partial \mathrm{S}_{\mathrm{total}} \geq 0\ \mathrm{J/K}$ for a process to be spontaneous, which is equivalent to $\partial \mathrm{U} \leq 0\ \mathrm{J}$ under conditions of constant volume and system entropy. However, if the process occurs under constant pressure and system entropy then $\partial \mathrm{H} \leq 0\ \mathrm{J}$. Now do you recall learning in Freshman Chemistry that Gibb's energy must be negative (i.e. $\partial \mathrm{G} \leq 0\ \mathrm{J}$) 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 $\partial \mathrm{S} = \frac{\partial \mathrm{q}_{\mathrm{rev}}}{\mathrm{T}}$, we must integrate it to generate a measurable result:

$$\Delta \mathrm{S} = \int \partial \mathrm{S} = \int \frac{\partial \mathrm{q}_{\mathrm{rev}}}{\mathrm{T}}$$

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

4.3.1 Changes in System Entropy.

Let's start with an isothermal reversible transition. Isothermal makes T constant, which means that the integral expression above can be simplified as:

$$\Delta S_{\mathrm{isoT,rev}} = \int \frac{\partial q_{\mathrm{rev}}}{T} = \frac{1}{T}\int \partial q_{\mathrm{rev}} = \frac{\Delta q_{\mathrm{rev}}}{T}$$

The isothermal reversible condition means that: $\Delta U = \Delta q_{\mathrm{rev}} + \Delta w_{\mathrm{rev}} = 0\ \mathrm{J}$, and thus:

$$\Delta q_{\mathrm{rev}} = -\Delta w_{\mathrm{rev}} = nRT \cdot \ln\left(\frac{V_f}{V_i}\right)$$

according to our learnings in Section 2.2. As a result:

$$\Delta S_{\mathrm{isoT,rev}} = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$$

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

We now move onto to adiabatic transitions. These calculations should be easy because $\partial q = 0\ \mathrm{J}$. Thus, there should be no change in the system entropy, regardless whether we are doing a reversible or irreversible transition. However, this isn't quite true because the definition of the change in entropy: $\partial S = \frac{\partial q_{\mathrm{rev}}}{T}$ is deficient. To analyze the situation, 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 we can state that there is first an isothermal change in volume (Path 1), for which we have already determined that: $\Delta S_1 = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. In the second step, there is a change in temperature under conditions of constant volume. To think practically, the only way to accomplish this is through a heat exchange, for which the relevant relationship is: $\partial q = C_V\, \partial T$ which is true whether the condition is reversible or not. Thus:

$$\Delta S_2 = \int \frac{\partial q_{\mathrm{rev}}}{T} = \int \frac{C_V\, \partial T}{T}$$

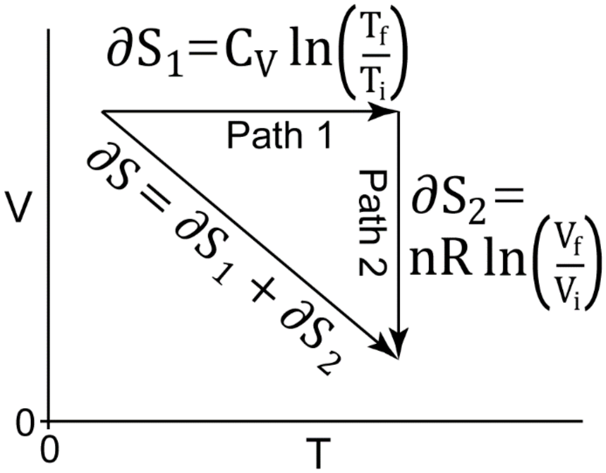


Figure 4.2. The change in entropy of an adiabatic process can be calculated using different paths.

The above needs to be converted into a definite integral, the limits of which have the units of the partial which is temperature. Thus:

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

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

$$\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right) + C_V \cdot \ln\left(\frac{T_f}{T_i}\right) \tag{4.5}$$

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

Now there are some nuances for applying the above equation for ΔS to adiabatic systems. For example, we already stated that it may appear $\Delta S_{ad} = 0\ \mathrm{J/K}$ for all adiabatic transitions because $\Delta q = 0\ \mathrm{J}$ for thermally insulated systems. To explore further we start with adiabatic reversible for which we have 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 on pg. 41. A small rearrangement yields: $\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^{\frac{nR}{C_V}}$ and then put this into the expression for ΔS:

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

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:

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

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

Thus, the system entropy change for adiabatic reversible transitions is $0\ \mathrm{J/K}$. In fact, if you are asked to analyze an adiabatic reversible transition and you correctly apply all the final and initial variables into your calculator, you will still find $\Delta S = 0\ \mathrm{J/K}$ (be careful with significant figures though).

The situation is not so simple for the adiabatic irreversible. 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:

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

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 the above expression. If calculated correctly, you will always find that $\Delta S_{\mathrm{ad,irrev}} > O\ J/K$. As a result, this reveals a small flaw with the expression $\partial S = \frac{\partial q_{rev}}{T}$, which implies that $\Delta S_{\mathrm{ad,irrev}} = 0\ \mathrm{J/K}$ which it is not. Chemical Engineers have long recognized this issue and resolved it by redefining changes in entropy as: $\partial S = \frac{\partial q_{rev}}{T} + \partial S_{added}$. The 2nd term is designed to account for this situation, although unfortunately it doesn't help you do the calculation.

4.3.2 Changes in Exterior Entropy. In the previous section we discussed how $\partial S_{total} \geq 0\ \mathrm{J/K}$ according to the 2nd Law, where the equality is for systems at equilibrium. We will now use this expression to determine how 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, $\partial S_{ext} = 0\ \mathrm{J/K}$ regardless of whether the transition is reversible or irreversible. Consequently, adiabatic reversible have a total entropy change of $\partial S_{tot} = \partial S_{ext} + \partial S = 0\ \mathrm{J/K}$. Likewise, the total change in entropy in the adiabatic irreversible case is $\partial S_{tot} = \partial S > 0\ J/K$, 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 $\partial q_{rev}$with the exterior. The resultant change in system entropy is $\frac{\partial q_{rev}}{T}$. Likewise, the exterior experiences a $-\partial q_{rev}$with the system and has a change of entropy of $-\frac{\partial q_{rev}}{T}$. Clearly, $\partial S_{tot} = \partial S + \partial S_{ext} = 0\ \mathrm{J/K}$; odd how this is also true for the adiabatic reversible. In fact, the definition of reversibility is $\partial S_{tot} = 0\ \mathrm{J/K}$. To be more specific, recall that we established the formula for isothermal change in system entropy, which means that the exterior change is: $\Delta S_{\mathrm{ext}} = -\Delta S = -\mathrm{nR} \cdot \ln\left(\frac{\mathrm{V_f}}{\mathrm{V_i}}\right)$. As for isothermal irreversible:

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

because $\partial \mathrm{S_{tot}} > 0\ J/K$ is the definition of an irreversible transition. Consequently, some middle-school algebra allows us to determine that: $\partial S_{\mathrm{ext}} > -\partial S$. Integration of this relationship yields: $\Delta S_{\mathrm{ext}} > -nR \cdot ln\left(\frac{\mathrm{V_f}}{\mathrm{V_i}}\right)$. It is odd that we do not have the ability to determine the exact change in $\Delta \mathrm{S_{ext}}$, rather we only know that it is greater than the reversible system 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 2.0, 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 contracting piston that lowers the system gas's entropy. What actor on the outside of the system is responsible for compressing the piston? If a cat did 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.

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

Table 4.1. Entropy changes for thermodynamic transitions.

4.4 The Car Engine, and the Carnot Cycle.

When civilization began, people survived by use of their hands. Farming meant pushing a plow, and although the discovery of the mule made this easier, it was the industrial revolution that demonstrated the utility of machines for work. Unlike mules, machines never tire and can be turned off and on at will, and their food is super-cheap. As this is oil, chemists have a unique role in understanding the inner workings of engines and their fuel.

At the beginning of this book it was stated that we burn fuel to do work. In other words, $\partial q \rightarrow \partial w$, and this direction of energy flow has profound implications for engine efficiency. First, we must consider how to power a practical 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. This worked, but 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 is one that can create work from heat in a cyclical process such that the end state is the same as the beginning. If this is confusing- think of a modern 4-stroke

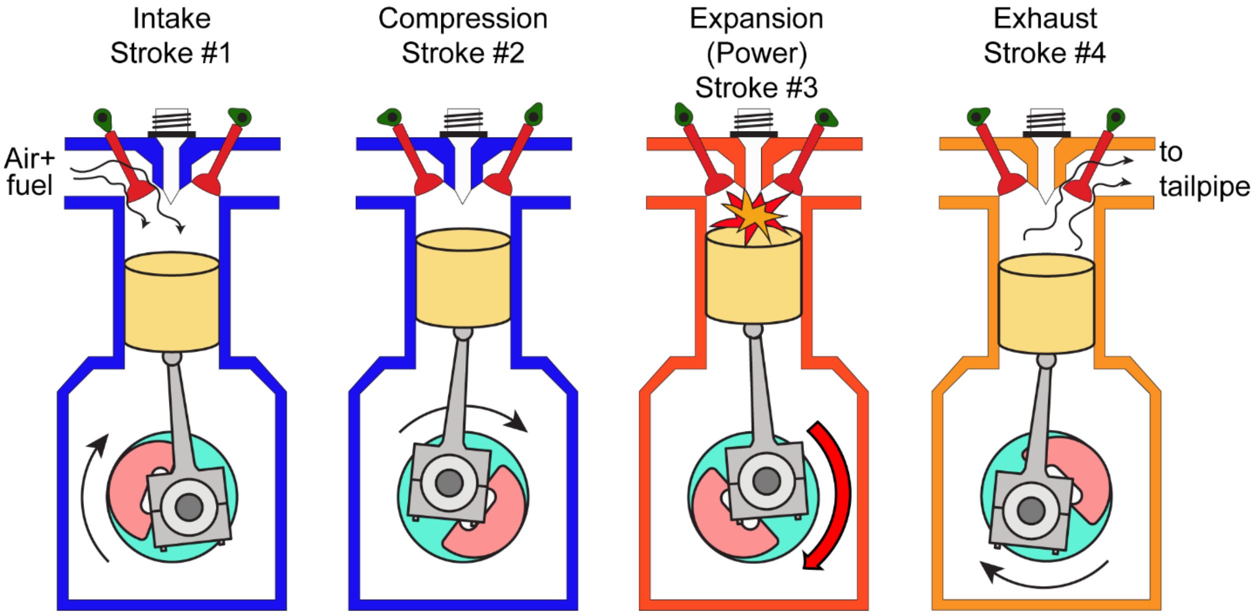


Figure 4.3. A four-stroke engine cycle first draws in a fuel / air mixture, compresses it, uses a spark plug to initiate the power stroke, and then exausts the waste gases into the tailpipe.

piston engine as shown in Figure 4.3. A mixture of petroleum and air is drawn inside, compressed, and then ignited by a sparkplug. The resulting expansion pushed the piston downward in the power stroke, and the resultant CO_2 gas and water vapor are pushed out into the tailpipe afterward. The piston is connected to the crankshaft that turns the car's wheels. The cyclical nature of the turning crankshaft returns the piston into the original state, which time more fuel and air are drawn in and burned as the process is repeated. One last thing to note- the 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

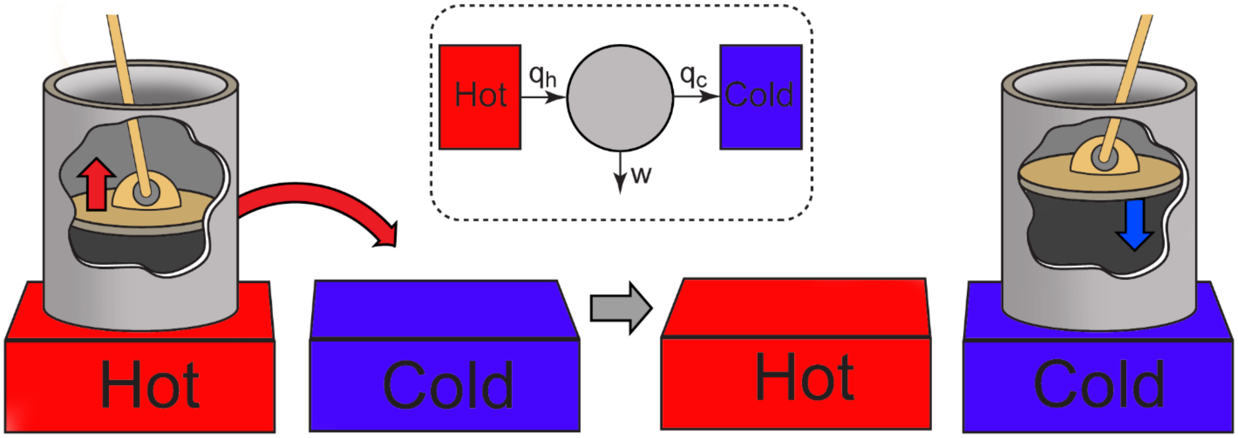


Figure 4.4. The interior of a piston expands when placed on a hot plate, and then compresses back into place when placed on a cold plate. This simple model allowed Carnot to view work as originating from a heat source that gets converted into work in a reciprocal manner as depicted by the interior diagram.

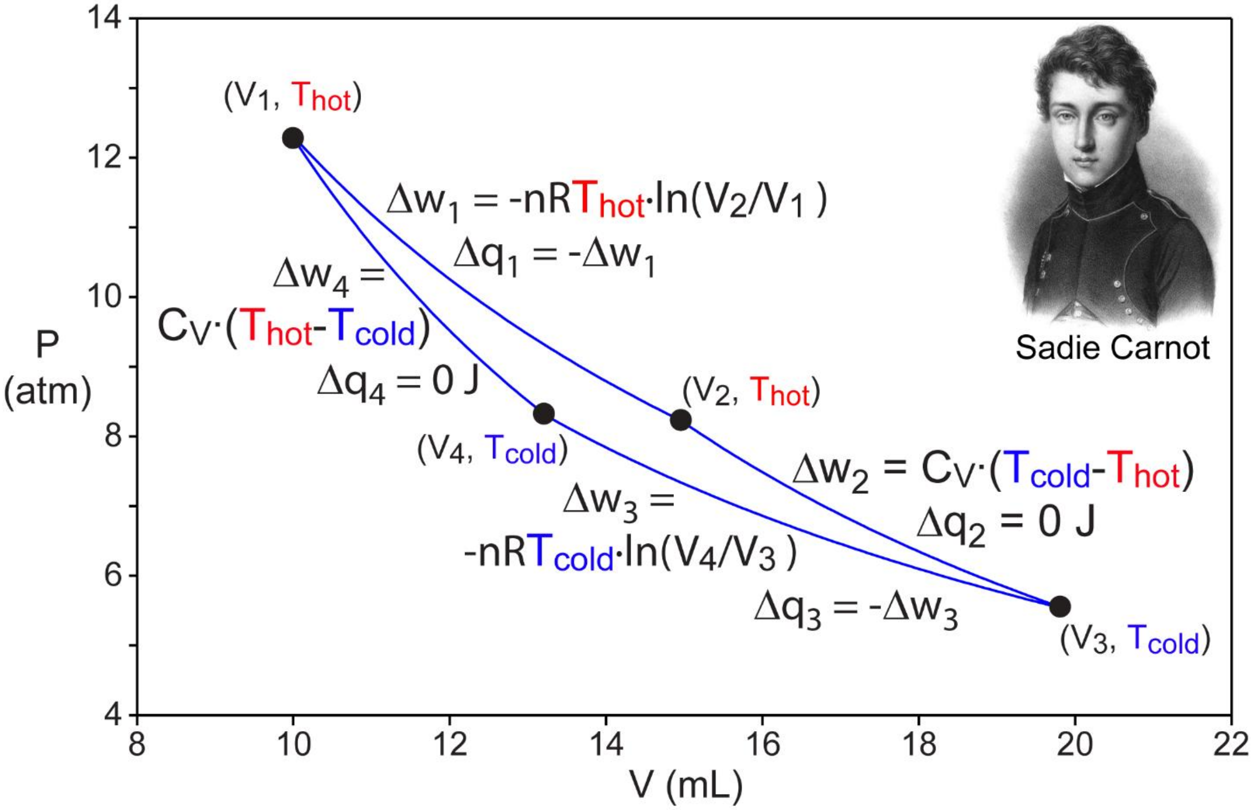


Figure 4.5. The Carnot Cycle for 3×10^{-3} mol of gas with T_{hot}=500 K and T_{cold}=446 K.

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 of processes occurring inside the piston of a reciprocating engine as 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. Of course adiabatic expansion cooled the cylinder to a lower temperature, T_{cold}. To compress the piston back to the original state, Carnot simply reversed the first two steps by using an isothermal reversible compression that releases heat followed by an adiabatic compression to return 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, and now we must perform some detailed analysis to understand the implications of a cyclical hot expansion followed by a cold compression. First, we can 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 $\Delta w_1 = -nRT_{hot} \cdot \ln\left(\frac{V_2}{V_1}\right)$; $\Delta w_2 = C_V \cdot (T_{cold} - T_{hot})$; $\Delta w_3 = -nRT_{cold} \cdot \ln\left(\frac{V_4}{V_3}\right)$; 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 2nd step:

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

and in the 4th 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 exaggerated example of the Carnot cycle shown in Figure 4.5. 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.

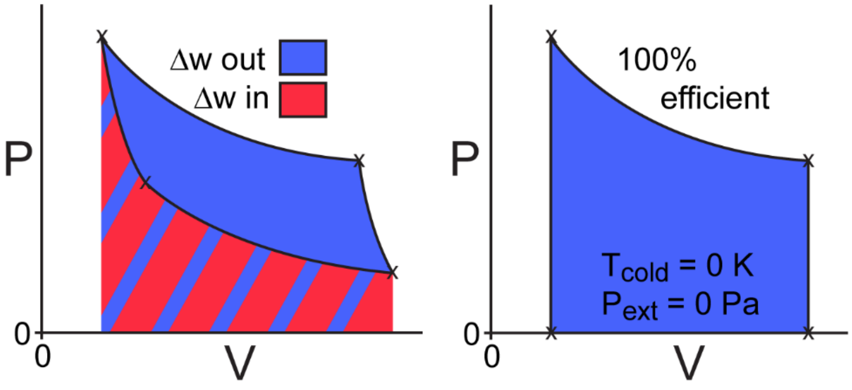


Figure 4.6. Left: An exaggerated view of the Carnot cycle shows that negative work is greater in magnitude than the positive. Right: The Carnot cycle is 100% efficient if the compression work is 0 J.

We can determine a few more important things such as the efficiency of the Carnot cycle. Here we must make some decisions on what is practically meant by efficiency. Since modern engines turn heat into work, it makes the most sense to determine the ratio of the total work divided by the heat: $\frac{\Delta w_{tot}}{\Delta q_{tot}}$. However, we have made a small phenomenological error as we shouldn't divide by the total heat. This is because we add the heat energy in the 1st expansion step, which takes action on our part. However, the 3rd compression step loses heat which doesn't take any effort. For example, in a car this is when the 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 the heat added in the 1st step: Δq_1. Note 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:

$$\text{Efficiency} = \left|\frac{\Delta w_{tot}}{\Delta q_1}\right| \tag{4.6}$$

Given that we have defined all of these terms, the efficiency is thus:

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

If you are following along but have lost track of a minus sign in the numerator, that is the effect of the absolute value. Regardless, this relationship shows that a Carnot cycle is never 100% efficient. This is a bit of a bummer, and it also shows us that some of the wacky Youtube videos of perpetually motion contraptions are impossible. So how can we make a machine at least more efficient? For one, we can do everything imaginable to make the ratio $\frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}}}$ 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 °C)?

There is another way to think of how a reciprocating engine is efficient, first by noting that if the cold block (i.e. car tailpipe) is at 0 K and the efficiency is 100%. How can a cold tailpipe affect mechanical motion or energy such that all heat energy is converted work? Recall that all this work is being performed by a gas. Using the perfect gas law: $\mathrm{PV = nRT_{cold}}$ with $\mathrm{T_{cold} = 0\ K}$ the pressures in the cold parts of the cycle (steps 3 and 4) are 0 kPa. As a result, the compression back to the original state is work against a vacuum, and since $\partial \mathrm{w} = -\mathrm{P_{ext}}\,\partial \mathrm{V}$, this isn't any work at all! This situation is depicted in Figure 4.6 right. This allows us to understand 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 summary of the lessons here 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. Upon closer analysis the efficiency of the transition $\left(\left|\frac{\Delta \mathrm{w_{tot}}}{\Delta \mathrm{q_1}}\right| = \frac{32.1\ \mathrm{J}}{100\ \mathrm{J}}\right)$ appears greater than allowed from our analysis of the Carnot cycle: $\left(1 - \frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}}}\right), \mathrm{T_{cold}} = 378\ \mathrm{K},\ \mathrm{T_{hot}} = 416\ \mathrm{K}$. However, the example problem doesn't follow a Carnot cycle and energy would be lost to regenerate the piston into its original state. Regardless, Problem 4.1 demonstrates consistency with the 2nd Law because ultimately the work is less in magnitude that the heat added.

4.4.2 Entropy of the Carnot Cycle. While we have demonstrated that a Carnot cycle cannot be practically 100% efficient, we now must ask the question: so what? Just like I wouldn't be too concerned with 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 from

Example Problem 4.1

Problem: If a filament is put inside an adiabatic 1 L piston full of N_2 gas at 1 atm pressure and room temperature (25 °C), one can input 100 J of energy. **a.** Initially the piston is fixed into position. Can you calculate how much the temperature rises? How much work is done? What is the new pressure?

b. Once released, the temperature of the piston will slowly drop as the volume reversibly expands to 1 atm. Can you calculate the final temperature? **c.** Now show that the reversible, adiabatic work is consistent with the 2nd Law. You need to know that $\mathrm{C_{V,m}} = 20.8\ \mathrm{J/K/mol}$ and $\mathrm{C_{P,m}} = 29.1\ \mathrm{J/K/mol}$ for nitrogen gas and assume perfect gas behavior.

Answer: a. First, we need to solve the number of moles of nitrogen: $\mathrm{n} = \frac{\mathrm{PV}}{\mathrm{RT}} = \frac{101.325\ \mathrm{Pa} \cdot 1\ \mathrm{L}}{8.314\ \mathrm{J/K/mol} \cdot 298.15\ \mathrm{K}} = 0.0409\ \mathrm{mol}$. The heat capacity is $0.0409\ \mathrm{mol} \times 20.8\mathrm{J/K/mol} = 0.850\ \mathrm{J/K}$, and thus the temperature rise is $\frac{\Delta \mathrm{q}}{\mathrm{C_V}} = 117.6\ \mathrm{K}$ (the final temperature is then 298.15K + 117.6K = 415.75K. The new pressure is $\mathrm{P} = \frac{\mathrm{nRT}}{\mathrm{V}} = \frac{0.0409\ \mathrm{mol} \cdot 8.314\ \mathrm{J/K/mol} \cdot 415.75\ \mathrm{K}}{1\ \mathrm{L}} = 141.4\ \mathrm{kPa}$. Of course there is no work done.

b. The piston will expand adiabatically and reversibly until the exterior pressure is 1 atm. Thus we need to use the following from the adiabatic equations of state: $\frac{\mathrm{P_f}}{\mathrm{P_i}} = \left(\frac{\mathrm{T_f}}{\mathrm{T_i}}\right)^{\frac{\mathrm{C_P}}{\mathrm{nR}}}$. Better yet: $\left(\frac{\mathrm{P_f}}{\mathrm{P_i}}\right)^{\frac{\mathrm{nR}}{\mathrm{C_P}}} = \frac{\mathrm{T_f}}{\mathrm{T_i}}$; plugging in values yields: $\left(\frac{101.325\ \mathrm{kPa}}{141.4\ \mathrm{kPa}}\right)^{\frac{0.0409\ \mathrm{mol} \cdot 8.314\ \mathrm{J/K/mol}}{0.0409\ \mathrm{mol} \cdot 29.1\mathrm{J/K/mol}}} = \left(\frac{\mathrm{T_f}}{415.75\mathrm{K}}\right)$. Solving for the final temperature yields $\mathrm{T_f}$ = 378 K.

c. We can now determine the work via: $\Delta \mathrm{w} = \mathrm{C_V} \Delta \mathrm{T} = 0.850\ \mathrm{J/K} \cdot (378\mathrm{K} - 415.75\mathrm{K}) = -32.1\ \mathrm{J}$.

each step. As steps 2 & 4 are adiabatic and reversible, there is no change in entropy at all (see Table 4.1 on pg. 76); thus $\Delta \mathrm{S}_{2+4} = 0\ \mathrm{J/K}$. As for steps 1 & 3, as these are isothermal reversible transitions:

$$\Delta \mathrm{S}_{1+3} = \mathrm{nR} \cdot \ln\left(\frac{\mathrm{V_2}}{\mathrm{V_1}}\right) + \mathrm{nR} \cdot \ln\left(\frac{\mathrm{V_4}}{\mathrm{V_3}}\right)$$

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:

$$\Delta S_{1+3} = -nR \cdot \ln\left(\frac{V_4}{V_3}\right) + nR \cdot \ln\left(\frac{V_4}{V_3}\right) = 0\ J/K$$

Consequently, the entropy change of the system throughout the cycle is $\Delta S_{1+2+3+4} = 0\ J/K$. Now we can consider the exterior changes in entropy. First, $\Delta S_{ext,2+4} = 0\ J/K$ since these steps are adiabatic, and likewise $\Delta S_{ext,1+3} = 0\ J/K$ 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. Heat flows from a hot source to a cold sink because of the relative changes in their entropies result in spontaneity. To demonstrate, we first assume that a hot block loses $-\partial q$ of thermal energy of which ∂q is gained by the cold block (the heat transaction is small enough that we consider the temperatures constant). The absolute values of the entropy changes for each system have the following relationship:

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

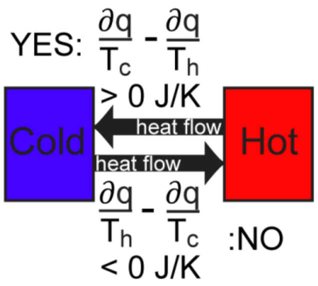


Figure 4.7. Total entropy causes heat to flow from hot to cold.

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 as shown in Figure 4.7. Your refrigerator is a freak of nature because heat flows the wrong way. As shown in the figure, 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:

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

Since you obey the laws of thermodynamics in your household, there is an interesting mechanism by which your refrigerator works such that the total entropy generated is positive. 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, which results in an expulsion of heat to the exterior. The liquid then flows past an expansion valve, resulting in a phase change that absorbs heat from the 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 negative ∂q_{hot} heat at T_{hot}.

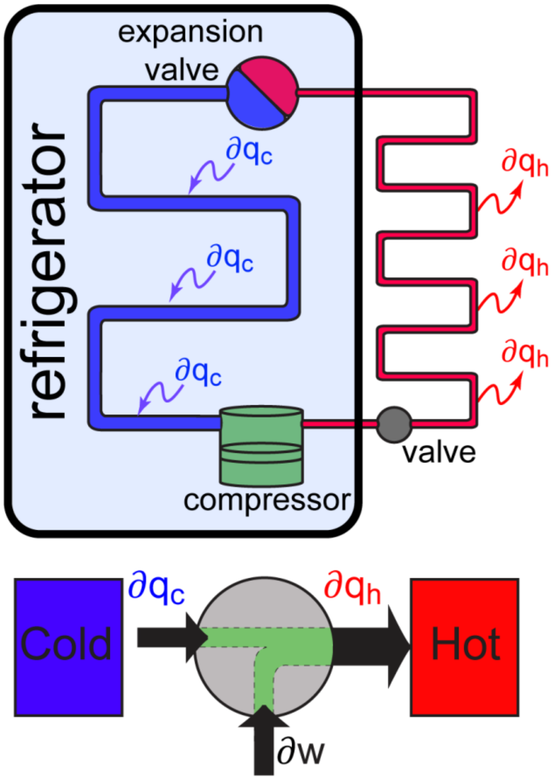


Figure 4.8. A refrigerator function by liquifying coolant through a compressor which then expands to absorb heat in the refrigerator interior.

To see how the system generates a net positive (or 0 J/K) of total entropy, we first note that there is an input of work 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, and thus greater entropy gain, compared to the losses by the refrigerator interior. In other words, $\partial q_{\text{cold}} < |\partial q_{\text{hot}}|$ (recall that ∂q_{hot} is negative and ∂q_{cold} is positive, so we have to make comparisons to $|\partial q_{\text{hot}}|$), and the entropy changes are:

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

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. Consequently, it is the compressor that represents the input of work, which contributes to the relative efficiency of the system as defined by the coefficient of performance. The efficiency of a refrigerator is defined by:

Example Problem 4.2

Problem: The standard temperature of a refrigerator is 4 °C, while a typical household is at 25 °C. If a typical refrigeration cycle consumes 50 kJ of energy,

Answer: TBD

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

A high COP is desirable, which means that COP is not quite the same thing as efficiency because it can be >100%. In fact, typical COPs are ~2→3. To derive the COP from these metrics of a refrigerator, we first note that conservation of energy requires:

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

as is obvious from Figure 4.8, and note we have to use the absolute value of Δq_{hot} because it's a negative quantity. This allows us to simplify the above:

$$\mathrm{COP} = \frac{\Delta q_{\mathrm{cold}}}{|\Delta q_{\mathrm{hot}}| - \Delta q_{\mathrm{cold}}}$$

To understand the COP better, we need to demonstrate a relationship between the two heat transactions (Δq_{hot} and $|\Delta q_{\mathrm{cold}}|$) 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:

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

(the absolute value of $-\Delta w_3$ results in the $\ln\left(\frac{V_3}{V_4}\right)$ term because $V_3 > V_4$). 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: $\frac{\Delta q_{\mathrm{cold}}}{|\Delta q_{\mathrm{hot}}|} = \frac{T_{\mathrm{cold}}}{T_{\mathrm{hot}}}$, or:

$$\Delta q_{\mathrm{cold}} = \frac{T_{\mathrm{cold}}}{T_{\mathrm{hot}}} |\Delta q_{\mathrm{hot}}|$$

Plugging the above into the equation for the COP yields:

$$\mathrm{COP} = \frac{\frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}}}|\Delta \mathrm{q_{hot}}|}{|\Delta \mathrm{q_{hot}}| - \frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}}}|\Delta \mathrm{q_{hot}}|} = \frac{\frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}}}}{1 - \frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}}}} = \frac{\mathrm{T_{cold}}}{\mathrm{T_{hot}} - \mathrm{T_{cold}}}$$

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 A Peltier system converts current directly into a temperature gradient, which is the thermoelectric effect. This was discovered because two wires, say copper and iron, if joined together in a closed loop and the two junctions have different temperatures, then current flows through the loop. In fact it is detectible by the magnetic field that is created (this is called the Seebeck effect). Unfortunately, they are ~1/4th as efficient (or worse) compared to conventional

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

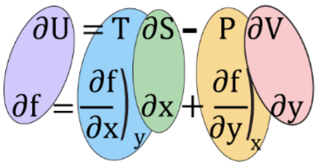
$$\partial \mathrm{U} = \partial \mathrm{q} + \partial \mathrm{w} = \mathrm{T}\,\partial \mathrm{S} - \mathrm{P}\,\partial \mathrm{V}$$

can be cast into the form of an exact differential:

$$\partial \mathrm{f(x,y)} = \left.\frac{\partial \mathrm{f}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \partial \mathrm{x} + \left.\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \partial \mathrm{y}$$

which is exact because $\left.\frac{\partial}{\partial \mathrm{y}}\left.\frac{\partial \mathrm{f}}{\partial \mathrm{x}}\right)_{\mathrm{y}}\right)_{\mathrm{x}} = \left.\frac{\partial}{\partial \mathrm{x}}\left.\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}}\right)_{\mathrm{y}}$

If we “line up” $\partial \mathrm{U}$ with $\partial \mathrm{f}$:



then we can see that f=U, x=S, and y=V, as as a result:

$$\left.\frac{\partial \mathrm{f}}{\partial \mathrm{x}}\right)_{\mathrm{y}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V}} = \mathrm{T}$$

and:

$$\left.\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\mathrm{P}$$

Now we can use the exactness of ∂U:

$$\frac{\partial}{\partial V}\frac{\partial U}{\partial S}\Big)_V\Big)_S = \frac{\partial}{\partial S}\frac{\partial U}{\partial V}\Big)_S\Big)_V$$

Where we insert $\frac{\partial U}{\partial S}\Big)_V = T$ on the left and $\frac{\partial U}{\partial V}\Big)_S = -P$ on the right:

$$\frac{\partial T}{\partial V}\Big)_S = \frac{-\partial P}{\partial S}\Big)_V \tag{4.7}$$

This 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 ∂H? Is there another Maxwell relationship? Starting with $\partial H = T\,\partial S + V\,\partial P$, which is an exact differential, and thus as before we see that $\frac{\partial}{\partial P}\frac{\partial H}{\partial S}\Big)_P\Big)_S = \frac{\partial}{\partial S}\frac{\partial H}{\partial P}\Big)_S\Big)_P$ which leads to:

$$\frac{\partial T}{\partial P}\Big)_S = \frac{\partial V}{\partial S}\Big)_P \tag{4.8}$$

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

4.6.1 Using Maxwell Relations. Maxwell relations based on U and H have components: $\frac{\partial T}{\partial V}\Big)_S$ and $\frac{\partial T}{\partial P}\Big)_S$, at constant system entropy S. Of all the thermodynamic processes, this is only true for adiabatic reversible transitions ($\Delta S = 0$ J/K). Furthermore, $\Delta S_{tot} = 0$ J/K as $\Delta S_{ext} = 0$ J/K due to the lack of heat exchange in adiabatic systems. Since there is no change in total entropy, the adiabatic reversible condition represents equilibrium, which allows us to examine $\frac{\partial T}{\partial V}\Big)_S$ and $\frac{\partial T}{\partial P}\Big)_S$ further to study systems at rest. What is interesting is that normally such derivatives as $\frac{\partial V}{\partial T}\Big)_P$, $\frac{\partial P}{\partial T}\Big)_V$, and $\frac{\partial P}{\partial V}\Big)_T$ are trivial using the perfect gas law; however, they do not apply to adiabatic systems. After all, P, V, and T are all simultaneously changing. As such, the purpose of this section is to determine $\frac{\partial V}{\partial T}\Big)_S$, $\frac{\partial P}{\partial T}\Big)_S$, and $\frac{\partial P}{\partial V}\Big)_S$ for systems at equilibrium.

4.6.1.1 Maxwell relation approach: $\frac{\partial V}{\partial T}\Big)_S$. First let us tackle $\frac{\partial V}{\partial T}\Big)_S$, although we have to note that there are multiple ways to perform such a derivation. We will use a Maxwell relation here, and in the next section we will demonstrate the same derivation using a slightly easier approach. Starting with:

$$\left.\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\left.\frac{\partial \mathrm{P}}{\partial \mathrm{S}}\right)_{\mathrm{V}}$$

This can be rearranged as: $\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = -\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{V}}$; so now we are trying to solve $-\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{V}}$. As $\partial \mathrm{U} = \mathrm{T}\,\partial \mathrm{S} - \mathrm{P}\,\partial \mathrm{V}$, we solve for the change in entropy as:

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

This expression can be divided by $\partial \mathrm{P}$, after which we apply the condition of constant volume:

$$-\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{V}} = -\left.\frac{1}{\mathrm{T}}\frac{\partial \mathrm{U}}{\partial \mathrm{P}}\right)_{\mathrm{V}} + \left.\frac{\mathrm{P}}{\mathrm{T}}\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{V}} = -\left.\frac{1}{\mathrm{T}}\frac{\partial \mathrm{U}}{\partial \mathrm{P}}\right)_{\mathrm{V}}$$

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

$$-\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{V}} = -\left.\frac{\mathrm{C_V}}{\mathrm{T}}\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{V}} = -\frac{\mathrm{C_V}}{\mathrm{T}}\frac{\mathrm{V}}{\mathrm{nR}}$$

where we used $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{V}} = \frac{\mathrm{V}}{\mathrm{nR}}$. As: $\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = -\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{V}}$ and $-\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{V}} = -\frac{\mathrm{C_V}}{\mathrm{P}}$, we can now show that:

$$\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = -\frac{\mathrm{C_V}}{\mathrm{P}}$$

Clearly the derivative is negative. This means that if one compresses the volume of an adiabatic system ($\partial \mathrm{V} = -$), then the temperature rises ($\partial \mathrm{T} = +$). 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: $\partial \mathrm{U} = \mathrm{T}\,\partial \mathrm{S} - \mathrm{P}\,\partial \mathrm{V}$. Under adiabatic reversible conditions $\partial \mathrm{U} = \mathrm{C_V}\,\partial \mathrm{T}$ and $\partial \mathrm{S} = 0\ \mathrm{J/K}$, leaving us with $\mathrm{C_V}\,\partial \mathrm{T} = -\mathrm{P}\,\partial \mathrm{V}$. A simple rearrangement yields $\frac{\partial \mathrm{T}}{\partial \mathrm{V}} = -\frac{\mathrm{P}}{\mathrm{C_V}}$, to which we must remember that we have already used the condition of constant entropy. Thus: $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\frac{\mathrm{P}}{\mathrm{C_V}}$, which rearranges to: $\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = -\frac{\mathrm{C_V}}{\mathrm{P}}$ as before.

4.6.1.3 Maxwell relation approach: $\left.\frac{\partial P}{\partial T}\right)_{S}$. If we start with Maxwell relation:

$$\left.\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{S}} = \left.\frac{\partial \mathrm{V}}{\partial \mathrm{S}}\right)_{\mathrm{P}}$$

the above can be rearranged as $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}}$. Thus, we need to determine $\left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}}$, and to do so we use $\partial \mathrm{H} = \mathrm{T}\,\partial \mathrm{S} + \mathrm{V}\,\partial \mathrm{P}$, to which we rearrange as $\partial \mathrm{S} = \frac{1}{\mathrm{T}}\partial \mathrm{H} - \frac{\mathrm{V}}{\mathrm{T}}\partial \mathrm{P}$. Next, we divide by the change in volume: $\frac{\partial \mathrm{S}}{\partial \mathrm{V}} = \frac{1}{\mathrm{T}}\frac{\partial \mathrm{H}}{\partial \mathrm{V}} - \frac{\mathrm{V}}{\mathrm{T}}\frac{\partial \mathrm{P}}{\partial \mathrm{V}}$ and now we apply constant pressure conditions:

$$\left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \frac{1}{\mathrm{T}}\left.\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{P}} + \frac{\mathrm{V}}{\mathrm{T}}\left.\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \frac{1}{\mathrm{T}}\left.\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{P}}$$

because $\frac{\mathrm{V}}{\mathrm{T}}\left.\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = 0\ \mathrm{Pa/K}$ due to the condition of constant pressure ($\partial \mathrm{P} = 0\ \mathrm{Pa}$). Substituting $\partial \mathrm{H} = \mathrm{C_P}\,\partial \mathrm{T}$:

$$\left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \frac{\mathrm{C_P}}{\mathrm{T}}\left.\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \frac{\mathrm{C_P}}{\mathrm{T}}\frac{\mathrm{P}}{\mathrm{nR}} = \frac{\mathrm{P}\cdot \mathrm{C_P}}{\mathrm{nRT}} = \frac{\mathrm{C_P}}{\mathrm{V}}$$

where we used $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \frac{\mathrm{P}}{\mathrm{nR}}$. As: $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}}$ and $\left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \frac{\mathrm{C_P}}{\mathrm{V}}$, we can now show that:

$$\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \frac{\mathrm{C_P}}{\mathrm{V}}$$

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 $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{S}}$ again starting with the change in enthalpy: $\partial \mathrm{H} = \mathrm{T}\,\partial \mathrm{S} + \mathrm{V}\,\partial \mathrm{P}$. Under adiabatic reversible conditions $\partial \mathrm{S} = 0\ \mathrm{J/K}$ and $\partial \mathrm{H} = \mathrm{C_P}\,\partial \mathrm{T}$, leaving us with $\mathrm{C_P}\,\partial \mathrm{T} = \mathrm{V}\,\partial \mathrm{P}$. A simple rearrangement yields: $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{S}} = \frac{\mathrm{V}}{\mathrm{C_P}}$. This of course rearranges to: $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \frac{\mathrm{C_P}}{\mathrm{V}}$ as we determined above.

4.6.1.5 $\left.\frac{\partial P}{\partial V}\right)_{S}$. Now for a harder one, $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right)_{\mathrm{S}}$. This is a bit more difficult because we don't have a good starting point. In this case, we use the Euler Chain which applied to the above is:

$$\left.\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}}\left.\frac{\partial \mathrm{P}}{\partial \mathrm{S}}\right)_{\mathrm{V}}$$

Here we can use two Maxwell relations, $\left.\frac{\partial \mathrm{S}}{\partial \mathrm{V}}\right)_{\mathrm{P}} = \left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{S}} = \frac{\mathrm{C_P}}{\mathrm{V}}$ and $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{S}}\right)_{\mathrm{V}} = -\left.\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = \frac{\mathrm{P}}{\mathrm{C_V}}$. Putting these together yields:

$$\left.\frac{\partial \mathrm{P}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\frac{\mathrm{C_P}}{\mathrm{C_V}}\frac{\mathrm{P}}{\mathrm{V}}$$

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). Like in the examples above, we already knew this, but it is 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 the result above: $\left.\frac{\partial P}{\partial V}\right)_S = -\frac{C_P}{C_V}\frac{P}{V}$ as $\frac{\partial P}{P} = -\frac{C_P}{C_V}\frac{\partial V}{V}$, we can integrate to find:

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

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. 41 demonstrates this exact derivation.

More Maxwell relation problems will be discussed in the next chapter, but first we must study two new energy functions generated by Legendre transformation. These are the Helmholtz and Gibbs energies.

Conclusion. Entropy is unequivocally the most important thermodynamic variable that exists. And now you see that energy is not as important as you one thought, all it does is allow you to measure total entropy changes more easily. From here on, we will now study constant temperature processes using energy equations that have temperature as a natural variable. And you will find that we have finally started to discuss that quantity you learned so much about in high school and Freshman chemistry- the Gibbs energy.

Problems: Numerical

1. A Roman Centurion must heat a sword (copper, mass of 5 kg, $C_{p,m}$ = 24.47 J/K/mol) from room temperature (25 °C) to 1000 °C to work out all the nicks and scratches. How much entropy is created by this? **(3 pts)**

2. A Roman Centurion needs to heat an iron anvil (mass of 1000 g, $C_{p,m}$ = 25.1 J/K/mol) from room temperature (25 °C) to 800 °C to do some metal work.

a. How much entropy is created by this? (Assume the volume of the anvil is constant) **(3 pts)**

b. Is entropy created by keeping the anvil at 800 °C? (hint, how do you keep the anvil hot?) **(2 pts)**

3. A typical car engine block weighs ~150 lbs and are typically made of iron ($C_{p,m}$ = 25.1 J/K/mol). **a.** How much entropy is created when the engine block heats from room temperature (25 °C) to 90 °C? **(4 pts)**

b. Let's say you're on a long drive of 60 miles. A Honda Civic will use about 3.1 gallons of gasoline and thus burn up 387,500 Btu to maintain the car engine block at 90 °C. How much entropy is generated by the heat necessary to maintain a constant engine block temperature? Hint: Btu is a "British Thermal Unit", and 1 Btu = 1055 Joules. **(4 pts)**

4. Gas in a box: I have 0.28 g of N_2 gas inside of my car engine's piston. When the gas burns, the temperature instantly jumps from 25 °C to 600 °C. In this short amount of time, the volume of the piston is the same, what is ΔS of the N_2 gas? The heat capacity $C_{v,m}$ of N_2 is 20.8 J/K/mol, assume it is not a function of temperature. **(4 pts)**

5. The molar enthalpy change of vaporizing ethanol is 38.6 kJ/mol at the boiling point (78.4 °C); likewise, it takes 23.35 kJ/mol for ammonia to boil at −33.34 °C. If you calculate ΔS for one mole of each of these substances, would you say that the values are *very* different from each other? Why might that be? **(4 pts)**

Hint: The entropy of a liquid is much, much smaller than a gas, and you are basically calculating S_{gas}-S_{liq}. Also, do perfect gases have very different entropies if P, T and V are the same (or very similar)?

6. The molar enthalpy change of vaporizing water is 40.7 kJ/mol at it's boiling point of 100 °C. What is the entropy change for 18.0 g of water turning from liquid to vapor? (Hint: Does boiling a pot of water occur under conditions of constant volume or pressure? Therefore, is there a relationship between ΔH and Δq?) **(4 pts)**

7. What are ΔS, $\Delta S_{exterior}$ and ΔS_{tot} for a mole of perfect gas that halves its volume isothermally and reversibly? **(5 pts)**

8. a. What are ΔS, $\Delta S_{exterior}$ and ΔS_{tot} for a mole of perfect gas that doubles its volume, gets compressed again, has a cat sit on top of it, explodes, implodes, is set on fire, is laughed at by the popular kids where every process is adiabatic and reversible? **(2 pts)**

b. What are ΔS, $\Delta S_{exterior}$ and ΔS_{tot} for a mole of a gas that has the volume doubled, and then halved isothermally and irreversibly? **(4 pts)**

9. What are ΔS, $\Delta S_{exterior}$ and ΔS_{tot} for a mole of perfect gas that doubles its volume isothermally and irreversibly at 90 °C? **(5 pts)**

10. What are ΔS, $\Delta S_{exterior}$ and ΔS_{tot} for by 0.5 mol of a gas ($C_{v,m}$ = 12.47 J/K/mol and $C_{p,m}$ = 20.8 J/K/mol) at 3 atm and 100 °C that irreversibly and adiabatically expands against an outside pressure of 1 atm? Note that this question is based on the example problem in Chapter 2; you can find the relevant volumes and temperatures there. **(6 pts)**

11. In the Chapter 3 Numerical question section, question #8 concerned an adiabatic irreversible transition and had 0.0101 moles of gas ($C_{v,m}$ = 20.8 J/K/mol) at initial conditions of: V_i = 0.3 L, T_i = 90 °C, and P_i = 1 atm. The final conditions were: V_f = 0.1214 L, T_f = 608.85 °C, and P_f = 6 atm. What is ΔS, $\Delta S_{exterior}$, and ΔS_{tot} for this transition? **(6 pts)**

12. What are ΔS, $\Delta S_{exterior}$ and ΔS_{tot} for by 1.5 mol of a gas ($C_{v,m}$ = 12.5 J/K/mol and $C_{p,m}$ = 20.8 J/K/mol) at 5 atm and 100 °C that irreversibly and adiabatically expands against an outside pressure of 1 atm, so that the final temperature is 292 K and the final volume is 36L? **(6 pts)**

13. Say an insulated piston is compressed to 2 atms of pressure; it has 1 mol of a gas ($C_{v,m}$ = 12.5 J/K/mol) and is at room temperature (25 °C). If you suddenly let go in a room at 1 atm of pressure, what are the final values of P, T, V, ΔU, ΔH, Δq, Δw, total ΔS, exterior ΔS, and the system ΔS? **(10 pts)**

Hint: remember that $\Delta U = C_v \times (T_f - T_i) = -P_{ext} \times (V_f - V_i)$; what you don't know is the final temperature and volume. You have to calculate these; note that the final volume is $n \times R \times T_f / 101.325$ kPa.

Problems: Theoretical or Explain in Words

1. When I look at a table of standard entropies, I see that Ar has $S_m°$ = 154.8 J/K/mol while N_2 has $S_m°$ = 191.6 J/K/mol. Is there a sensible reason why that is? (Hint: Think heat about the heat capacities and how you calculate S° at 298.15 K) **(5 pts)**

2. In the formula for entropy change of a system: $\Delta S = C_V \cdot \ln\left(\frac{T_f}{T_i}\right) + nR \cdot \ln\left(\frac{V_f}{V_i}\right)$, what do you get for ΔS if you insert the adiabatic equation of state: $\frac{V_f}{V_i} = \left(\frac{T_i}{T_f}\right)^{\frac{C_V}{nR}}$? **(10 pts)**

Hint: substitute $\left(\frac{T_i}{T_f}\right)^{\frac{C_V}{nR}}$ for $\frac{V_f}{V_i}$ and simplify the answer. You should be able to give me a number!

3. In the formula for entropy change of a system: $\Delta S = C_V \cdot \ln\left(\frac{T_f}{T_i}\right) + nR \cdot \ln\left(\frac{V_f}{V_i}\right)$, can you show how to derive the "pressure" form: $\Delta S = C_P \cdot \ln\left(\frac{T_f}{T_i}\right) + nR \cdot \ln\left(\frac{P_i}{P_f}\right)$? Hint: start with the perfect gas law for the volumes; $\ln\left(\frac{a \cdot c}{b \cdot d}\right) = \ln\left(\frac{a}{b}\right) + \ln\left(\frac{c}{d}\right)$, and $C_V + nR = C_P$. **(10 pts)**

4. Does the temperature of a gas increase with increasing pressure at constant entropy (i.e. adiabatic and reversible)? Hint: you're looking for $\left.\frac{\partial T}{\partial P}\right)_S$. Start with the fact that $\partial H = C_P\,\partial T$ under adiabatic conditions and at the same time $\partial H = T\,\partial S + V\,\partial P$. **(5 pts)**

5. If the internal energy (U) of a perfect gas is: $\partial U = T\,\partial S - P\,\partial V$, can you prove that $\left.\frac{\partial V}{\partial T}\right)_S = \frac{-C_V}{P}$ given that $\left.\frac{\partial U}{\partial T}\right)_S = C_V$? **(5 pts)**

6. Can you re-derive the adiabatic equation of state $\frac{V_f}{V_i} = \left(\frac{T_i}{T_f}\right)^{\frac{C_V}{nR}}$ from $\left.\frac{\partial V}{\partial T}\right)_S = \frac{-C_V}{P}$? **(7 pts)**

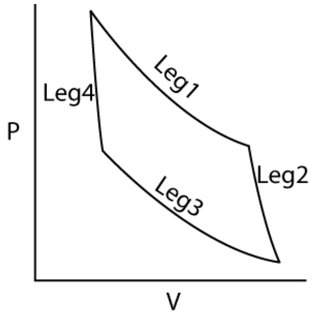
7. Does the internal energy (U) of a perfect gas go up or down with increasing pressure under adiabatic, reversible conditions (i.e. at constant entropy)? Hint: you're looking for $\left.\frac{\partial U}{\partial P}\right)_S$, and under conditions of constant entropy, the transition must be adiabatic and reversible. As such: $\partial U = C_V\,\partial T$, and $\left.\frac{\partial T}{\partial P}\right)_S = \frac{V}{C_P}$. **(7 pts)**

8. Tell me in words- why does it make sense that internal energy increases with increasing pressure at constant entropy? Hint: think about how you increase the pressure, and don't forget the equipartition theorem. **(5 pts)**

9. If the enthalpy (H) of a perfect gas is: $\partial H = T\,\partial S + V\,\partial P$, can you prove that $\left.\frac{\partial P}{\partial T}\right)_S$ is positive given that $\left.\frac{\partial H}{\partial T}\right)_S = C_P$? **(7 pts)**

10. Starting with the Clausius Inequality, $\partial S \geq \frac{\partial q}{T}$, can you prove that, under conditions of constant pressure and entropy, for the total entropy to increase, $\partial H < 0\,J$? Hint, first look in your notes for how we worked the same problem for U at constant S and V. **(7 pts)**

11. State whether Δw, Δq, ΔU and ΔS is positive, 0, or negative for each leg of the Carnot cycle. Use this diagram (I know the slopes of the sides may be a little bit off):



	Δw	Δq	ΔU	ΔS
Leg 1:				
Leg 2:				
Leg 3:				
Leg 4:				

Chapter 5: Helmholtz and Gibbs Energy

Entropy is very important to understanding how all processes, both chemical and mechanical, practically occur in nature. By "occur", we mean spontaneous and has a $\Delta S_{tot} > 0\,J/K$. 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 that energy are held constant. Thus, spontaneous means that $\Delta U < 0\,J$ if S and V are constant while $\Delta H < 0\,J$ if S and P are constant. The constant entropy condition is only true for adiabatic and reversible, which describes a system at equilibrium. But what about all the other types of transitions (irreversible and isothermal)?

Consider the following question- is the world adiabatic or isothermal? While you may be thinking that isothermal can be eliminated because temperature changes during the seasons, it is also true that the Earth is not encapsulated in glass wool like the flask in Figure 2.0. For the most part, we live in an isothermal system. 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 dictates whether a process is spontaneous under isothermal, constant pressure environment, because clearly 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 now we need to derive 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: $\partial U = T\boldsymbol{\partial S} - P\boldsymbol{\partial V}$; thus U(S,V). The conjugate variable of S is T and the conjugate of V is –P. In Sec. 3.3 that we showed how to transform away internal energy's natural dependence on volume by defining the enthalpy function: $H = U + PV$. This is a Legendre transform, and involves taking a function (U) and subtracting the natural variable times its conjugate $-(-PV) = +PV$. The natural variables are discerned by examination of the change in enthalpy: $\partial H = T\boldsymbol{\partial S} + V\boldsymbol{\partial P}$. Clearly the natural variables are S and P and thus H(S,P). Now let's use a Legendre transform to take away internal energy's dependence on entropy and place it on temperature. Let's start by defining a new function, which we will call Helmholtz energy A via:

$$\mathrm{A = U - TS} \tag{5.1}$$

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

$$\partial \mathrm{A} = \partial \mathrm{U} - \partial(\mathrm{TS}) = -\mathrm{P}\,\partial \mathrm{V} + \mathrm{T}\,\partial \mathrm{S} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T} = -\mathrm{P}\boldsymbol{\partial}\mathbf{V} - \mathrm{S}\boldsymbol{\partial}\mathbf{T} \tag{5.2}$$

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

Like a new car, we can how take Helmholtz energy out for a ride 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. Heat is important because we power the planet by burning things, including nuclear fuel. What about work? Work is also pretty important, and the maximum out of a system is the reversible work which is $\partial \mathrm{w_{rev}} = -\mathrm{P}\,\partial \mathrm{V}$. Thus it is clear that Helmholtz energy is reversible work under conditions of constant temperature (its natural variable), since $\partial \mathrm{A} = -\mathrm{P}\,\partial \mathrm{V}$. In fact, the reason that 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 conditions when 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 2nd 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 plus surroundings; please recall that $-{}^{\partial \mathrm{q}}/_{\mathrm{T}}$ is the change in the surrounding's entropy:

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

If we multiply the above by –T:

$$\partial \mathrm{q} - \mathrm{T}\,\partial \mathrm{S} \leq 0\ \mathrm{J}$$

Although this doesn't make sense now, let us make a change by subtracting and adding $\mathrm{S}\,\partial \mathrm{T}$:

$$\partial \mathrm{q} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T} + \mathrm{S}\,\partial \mathrm{T} \leq 0\ \mathrm{J}$$

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

$$\partial \mathrm{A} = \partial \mathrm{U} - \partial(\mathrm{TS}) = \partial \mathrm{U} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T}$$

and since $\partial \mathrm{U} = \partial \mathrm{q} - \mathrm{P}\,\partial \mathrm{V}$:

$$\partial \mathrm{A} = \partial \mathrm{q} - \mathrm{P}\,\partial \mathrm{V} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T}$$

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

$$\partial \mathrm{A} = \partial \mathrm{q} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T}$$

And now we can insert $\partial \mathrm{A}$ into the expression above ($\partial \mathrm{q} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T} + \mathrm{S}\,\partial \mathrm{T} \leq 0\ \mathrm{J}$) as:

$$\partial \mathrm{A} + \mathrm{S}\,\partial \mathrm{T} \leq 0\ \mathrm{J}$$

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 $\partial \mathrm{T} = 0\ \mathrm{K}$ and thus:

$$\partial \mathrm{A} \leq 0\ \mathrm{J}$$

Since this derivation began with $\partial \mathrm{S}_{\mathrm{tot}} \geq 0\ \mathrm{J/K}$, the above is basically statin the same thing, that being for a process to be spontaneous under conditions of constant volume and temperature that 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 and 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 °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. Here is a solution to the problem- don't do chemical reactions in closed vessels. But now we need a new definition of energy.

5.2 Gibbs Energy. Gibbs energy is the ultimate Legendre transform; 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:

$$\mathrm{G} = \mathrm{U} + \mathrm{PV} - \mathrm{TS} \tag{5.3}$$

We can establish the natural variables of this new function by determining the change in the function:

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

Since $\partial \mathrm{U} = -\mathrm{P}\,\partial \mathrm{V} + \mathrm{T}\,\partial \mathrm{S}$ and $\partial(\mathrm{PV}) = \mathrm{P}\,\partial \mathrm{V} + \mathrm{V}\,\partial \mathrm{P}$ (likewise for TS):

$$= -\mathrm{P}\,\partial \mathrm{V} + \mathrm{T}\,\partial \mathrm{S} + \mathrm{P}\,\partial \mathrm{V} + \mathrm{V}\,\partial \mathrm{P} - \mathrm{T}\,\partial \mathrm{S} - \mathrm{S}\,\partial \mathrm{T}$$

which simplifies to:

$$\partial \mathrm{G} = \mathrm{V}\boldsymbol{\partial}\mathbf{P} - \mathrm{S}\boldsymbol{\partial}\mathbf{T} \tag{5.4}$$

We can derive the same faster if we started with enthalpy, since $\mathrm{H} = \mathrm{U} + \mathrm{PV}$ and H already has P as a natural variable. We simply Legendre transform away the entropy dependence of enthalpy:

$$\mathrm{G} = \mathrm{H} - \mathrm{TS} \tag{5.5}$$

from which we can see that:

$$\partial\mathrm{G} = \partial\mathrm{H} - \partial(\mathrm{TS}) = \mathrm{V}\,\partial\mathrm{P} + \mathrm{S}\,\partial\mathrm{T} - \mathrm{T}\,\partial\mathrm{S} - \mathrm{S}\,\partial\mathrm{T}$$

which simplifies to:

$$\partial\mathrm{G} = \mathrm{V}\boldsymbol{\partial}\mathbf{P} - \mathrm{S}\boldsymbol{\partial}\mathbf{T}$$

as before. Clearly 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, $\partial\mathrm{G} = \mathrm{V}\,\partial\mathrm{P}$. Note that this isn't reversible work, or, is it? To investigate further, first calculate the change in G with respect to V at constant T:

$$\left.\frac{\partial\mathrm{G}}{\partial\mathrm{V}}\right)_{\mathrm{T}} = \mathrm{V}\left.\frac{\partial\mathrm{P}}{\partial\mathrm{V}}\right)_{\mathrm{T}}$$

If we insert the perfect gas law then:

$$\left.\frac{\partial\mathrm{G}}{\partial\mathrm{V}}\right)_{\mathrm{T}} = \mathrm{V}\left(\frac{-\mathrm{nRT}}{\mathrm{V}^2}\right) = \mathrm{V}\left(\frac{-\mathrm{P}}{\mathrm{V}}\right) = -\mathrm{P}$$

Since we can "juggle" partials algebraically, we see that:

$$\partial\mathrm{G} = -\mathrm{P}\,\partial\mathrm{V}$$

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

Last, a negative change in Gibbs energy is the same as a positive change in total entropy if the process under consideration is at constant temperature and pressure. 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) times four conditions (isothermal or adiabatic × reversible or irreversible). This lends itself to 48 types of thermodynamic calculations, although this isn't quite so bad because changes in state variables (U, H, A, G, S) can be calculated the same way regardless of the conditions due to exactness. We will now discuss calculating $\Delta\mathrm{A}$ and $\Delta\mathrm{G}$ for gas expansion / contraction problems, although as we demonstrate below there are some problems arise that don't have simple solutions. This chapter is also the last holdout for these types of questions, because in Chapter 6 and beyond we will apply all these thermodynamic calculations to real chemical species.

5.3.1 Thermodynamic Calculations. We will examine how to calculate changes in Gibbs and Helmholtz energies for gas work-type calculations under isothermal and adiabatic conditions. As you can imagine, the fact that these are state variables means that there are some generalities that make these problems easier. For example, the changes in Helmholtz and Gibbs energies for either reversible or irreversible isothermal transitions are simple to determine because they are both equal to the reversible work: $\partial\mathrm{A} = \partial\mathrm{G} = \partial\mathrm{w}_{\mathrm{rev}}$.

We run into some problems for the adiabatic cases. Concerning the adiabatic reversible which occurs at a constant system entropy ($\partial S = 0\ \mathrm{J/K}$), we can see from:

$$\partial\mathrm{G} = \partial\mathrm{H} - \partial(\mathrm{TS}) = \partial\mathrm{H} - \mathrm{S}\,\partial\mathrm{T} - \mathrm{T}\,\partial\mathrm{S} = \partial\mathrm{H} - \mathrm{S}\,\partial\mathrm{T}$$

Since $\partial\mathrm{H} = \mathrm{C_P}\,\partial\mathrm{T}$ under adiabatic reversible conditions:

$$\partial\mathrm{G} = \mathrm{C_P}\,\partial\mathrm{T} - \mathrm{S}\,\partial\mathrm{T}$$

the change in Gibbs energy can be calculated once the change in temperature has been determined. Likewise, $\partial\mathrm{A} = \mathrm{C_V}\,\partial\mathrm{T} - \mathrm{S}\,\partial\mathrm{T}$. However, the absolute value of the entropy of the system (S) must be known as well. The absolute entropy of any chemical entity can be determined to the 3rd Law. However, this is a bit complex and is thus the subject of the next chapter, so we won't consider this further.

Last, the adiabatic irreversible is very problematic because they do not occur under conditions of constant system entropy. Thus, for $\partial\mathrm{G} = \mathrm{C_P}\,\partial\mathrm{T} - \partial(\mathrm{TS})$ both S and T are simultaneously changing because entropy is a function of temperature. This is a more difficult problem and requires some help from a computer. We also question the value of knowing the changes of Gibbs and Helmholtz energies for adiabatic transitions. For an adiabatic process to be spontaneous is it true that $\Delta\mathrm{A} < 0\ J$ or $\Delta\mathrm{G} < 0\ J$? If not, do we really need to care about these types of energies?

5.3.2 Thermodynamic Proofs. Up or down? 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 The Gibbs-Helmholtz Equation. We have stated several times that the Earth (and most processes on this planet) is a constant temperature and pressure system. As a result, if a process has a negative change in Gibbs energy, then the total entropy is increasing, and the process must be spontaneous. Thus, calculating 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 most relevant at constant temperature. It's because a chemical process can be conducted at constant temperature, but we never said at what temperature. If a reaction is not spontaneous at 25 ºC, could it be spontaneous if we raised the temperature to 100 ºC (and then held the temperature constant)? This is something that we might want to know. We will thus calculate $\left.\frac{\partial G}{\partial T}\right)_P$, starting with constant pressure ($\partial P = 0$ Pa) just to make the derivation easier. We have already established that:

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

and thus $\left.\frac{\partial G}{\partial T}\right)_P = -S$. Since entropy is always positive according to the 3rd Law (see Chapter 6), Gibbs energy goes down with increasing temperature. This information on its own gives us much insight- 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. As we will see in Chapter 6, it is very difficult to know what the absolute entropy of a substance is. Basically, there is no entropy "thermometer", and even worse S itself is a function of temperature. Thus, we need to try to insert something in for entropy to make the measurement of $\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$ easier. Starting with $\mathrm{G} = \mathrm{H} - \mathrm{TS}$, we can see that $\mathrm{S} = \frac{\mathrm{H}-\mathrm{G}}{\mathrm{T}}$, which then gives us: $\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \frac{\mathrm{G}-\mathrm{H}}{\mathrm{T}}$. Unfortunately, we are mathematically stuck because we have $\partial\mathrm{G}$ on the left side of the equation and G on the right. We must have all the G's on the left side of the equation or we can't integrate $\partial\mathrm{G}$ properly, and unfortunately there is no easy way to algebraically factor G out of $\frac{\mathrm{G}-\mathrm{H}}{\mathrm{T}}$.

It turns out that we can 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 T is always a positive quantity, and thus it won't affect whether G goes up ($\partial\mathrm{G}$ is positive) or goes down ($\partial\mathrm{G}$ is negative) with increasing temperature. Let us start with:

$$\left.\frac{\partial \, {}^{\mathrm{G}}\!/_{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \frac{1}{\mathrm{T}}\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} - \frac{\mathrm{G}}{\mathrm{T}^2} = \frac{1}{\mathrm{T}}\left(\frac{\partial \mathrm{G}}{\partial \mathrm{T}} - \frac{\mathrm{G}}{\mathrm{T}}\right)$$

which comes from the product rule identity $\frac{\partial(\mathrm{f}\cdot\mathrm{z})}{\partial \mathrm{x}} = \mathrm{z}\frac{\partial \mathrm{f}}{\partial \mathrm{x}} + \mathrm{f}\frac{\partial \mathrm{z}}{\partial \mathrm{x}}$, where f=G, x=T, and z=1/T. Next, if we go back to $\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \frac{\mathrm{G}-\mathrm{H}}{\mathrm{T}}$ and make some rearrangements: $\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \frac{\mathrm{G}}{\mathrm{T}} - \frac{\mathrm{H}}{\mathrm{T}}$ we find that:

$$\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} - \frac{\mathrm{G}}{\mathrm{T}} = -\frac{\mathrm{H}}{\mathrm{T}}$$

This is inserted into our earlier expression:

$$\left.\frac{\partial \, {}^{\mathrm{G}}\!/_{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = \frac{1}{\mathrm{T}}\left(\left.\frac{\partial \mathrm{G}}{\partial \mathrm{T}}\right)_{\mathrm{P}} - \frac{\mathrm{G}}{\mathrm{T}}\right) = \frac{1}{\mathrm{T}}\left(-\frac{\mathrm{H}}{\mathrm{T}}\right) = -\frac{\mathrm{H}}{\mathrm{T}^2}$$

which is the Gibbs-Helmholtz equation. This will be very important in our further developments on phase transitions and colligative properties in later chapters. For now, let's use it for our original on whether we should heat up a chemical reaction that isn't "going" (i.e. is non-spontaneous because of a positive ΔG). For a reaction, we take the Gibbs-Helmholtz equation $\left.\frac{\partial \, {}^{\mathrm{G}}\!/_{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -\frac{\mathrm{H}}{\mathrm{T}^2}$ and we re-write it as:

$$\left.\frac{\partial \, {}^{\Delta\mathrm{G}}\!/_{\mathrm{T}}}{\partial \mathrm{T}}\right)_{\mathrm{P}} = -\frac{\Delta\mathrm{H}}{\mathrm{T}^2} \tag{5.6}$$

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

$$\partial \mathrm{f} = \left.\frac{\partial \mathrm{f}}{\partial \mathrm{x}}\right)_{\mathrm{y}} \partial \mathrm{x} + \left.\frac{\partial \mathrm{f}}{\partial \mathrm{y}}\right)_{\mathrm{x}} \partial \mathrm{y}$$

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

$$\partial \mathrm{U} = \mathrm{T}\,\partial \mathrm{S} - \mathrm{P}\,\partial \mathrm{V}$$

therefore $\left.\frac{\partial}{\partial \mathrm{V}} \left.\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V}}\right)_{\mathrm{S}} = \left.\frac{\partial}{\partial \mathrm{S}} \left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}}\right)_{\mathrm{V}}$, and since $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{S}}\right)_{\mathrm{V}} = \mathrm{T}$ and $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = -\mathrm{P}$, then:

$$\left.\frac{\partial \mathbf{T}}{\partial \mathbf{V}}\right)_{\mathbf{S}} = -\left.\frac{\partial \mathbf{P}}{\partial \mathbf{S}}\right)_{\mathbf{V}} \tag{5.7}$$

Likewise $\partial \mathrm{H} = \mathrm{T}\,\partial \mathrm{S} + \mathrm{V}\,\partial \mathrm{P}$, which leads to $\left.\frac{\partial}{\partial \mathrm{P}} \left.\frac{\partial \mathrm{H}}{\partial \mathrm{S}}\right)_{\mathrm{P}}\right)_{\mathrm{S}} = \left.\frac{\partial}{\partial \mathrm{S}} \left.\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{S}}\right)_{\mathrm{P}}$ and thus:

$$\left.\frac{\partial \mathbf{T}}{\partial \mathbf{P}}\right)_{\mathbf{S}} = \left.\frac{\partial \mathbf{V}}{\partial \mathbf{S}}\right)_{\mathbf{P}} \tag{5.8}$$

More interesting relationships are derived from:

$$\partial \mathrm{A} = -\mathrm{S}\,\partial \mathrm{T} - \mathrm{P}\,\partial \mathrm{V} \text{ and } \partial \mathrm{G} = -\mathrm{S}\,\partial \mathrm{T} + \mathrm{V}\,\partial \mathrm{P}$$

Such as:

$$\left.\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{T}} = \left.\frac{\partial \mathbf{P}}{\partial \mathbf{T}}\right)_{\mathbf{V}} \tag{5.9}$$

and:

$$\left.\frac{\partial \mathbf{S}}{\partial \mathbf{P}}\right)_{\mathbf{T}} = -\left.\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{\mathbf{P}} \tag{5.10}$$

These last two relations 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 $\left.\frac{\partial S}{\partial P}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_P$? The derivative on the right is easy to determine using the perfect gas equation: $-\left.\frac{\partial V}{\partial T}\right)_P = -\frac{\partial^{nRT}/_P}{\partial T} = -\frac{nR}{P}$. 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: $\Delta S = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$. And although we have already established that fact, we can here re-derive that relationship using: $\left.\frac{\partial S}{\partial P}\right)_T = -\frac{nR}{P}$ by rearranging this as: $\partial S = -\frac{nR}{P}\partial P$ and then integrating: $\int_{S_i}^{S_f}\partial S = \Delta S = -\int_{P_i}^{P_f}\frac{nR}{P}\partial P = nR \cdot \ln\left(\frac{P_i}{P_f}\right)$. If we insert the perfect gas equation for the pressure we find $\Delta S = nR \cdot \ln\left(\frac{^{nRT}/_{V_i}}{^{nRT}/_{V_f}}\right) = nR \cdot \ln\left(\frac{V_f}{V_i}\right)$ as above. If we had started with the Helmholtz Maxwell relation: $\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$ we would have determined the same in just one step!

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

$\boldsymbol{\left.\frac{\partial S}{\partial V}\right)_T}$**.** 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 this to $\left.\frac{\partial S}{\partial V}\right)_T = -\alpha V \left.\frac{\partial P}{\partial V}\right)_T$. Now we also know that $\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T$ so $\frac{1}{\kappa_T} = -V\left.\frac{\partial P}{\partial V}\right)_T$ so $\left.\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\kappa_T}$.

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

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.

Problems: Numerical

1. 3.2 g of O_2 gas (molar $C_{v,m}$=21.1 J/K/mol) at 30 °C expands adiabatically and reversibly from 1.24 L to 2.49 L. Please calculate: Δq, n, C_v, ΔT, Δw, ΔU, ΔH, ΔS, $\Delta S_{exterior}$, and ΔS_{total}. **(10 pts)**

2. 9.0 g of H_2O gas (molar $C_{v,m}$=25.3 J/K/mol) at 125 °C expands isothermally and reversibly from 5.44 L to 16.3 L. Please calculate: n, ΔT, ΔU, ΔH, Δq, C_v, Δw, ΔS, $\Delta S_{exterior}$, and ΔS_{total}, ΔA, and ΔG. **(10 pts)**

3. 0.90 g of H_2O gas (molar $C_{v,m}$=25.3 J/K/mol) at 100 °C expands isothermally and reversibly from 0.765 L to 1.53 L. Please calculate: n, ΔT, ΔU, ΔH, Δq, C_v, Δw, ΔS, $\Delta S_{exterior}$, and ΔS_{total}, ΔA, and ΔG. **(10 pts)**

4. 8.0 g of Ar gas (molar $C_{v,m}$=12.47 J/K/mol) at 25 °C contracts isothermally and reversibly from 2L to 1 L. Please calculate: n, ΔU, ΔH, Δq, C_v, ΔT, Δw, ΔS, $\Delta S_{exterior}$, and ΔS_{total}, ΔA, and ΔG. **(10 pts)**

5. 14.0 g of N_2 gas (molar $C_{v,m}$=29.1 J/K/mol) at 273.15 K in a 5L piston expands isothermally against a constant pressure of 1 atm. Please calculate: ΔT, n, ΔV, ∂w, ∂q, ΔU, ΔH, ΔS, ΔA and ΔG. **(10 pts)**

6. 1.4 g of N_2 gas (molar $C_{v,m}$=29.1 J/K/mol) at 273.15 K expands adiabatically and reversibly from 1.22 to 2.44 L. Please calculate: Δq, n, C_v, ΔT, Δw, ΔU, ΔH, ΔS, $\Delta S_{exterior}$, and ΔS_{total}. (hint, the order of these variables is not random.) **(10 pts)**

7. 0.9 g of H_2O gas at 0 °C contracts adiabatically and irreversibly starting from 2.24 L in a room at atmospheric pressure (1 atm); the heat capacity at constant volume is $C_{v,m}$ = 26.3 J/K/mol. Please calculate: Δq, n, C_v, ΔT, V_{final}, Δw, ΔU, ΔH, ΔS, $\Delta S_{exterior}$, and ΔS_{total}. **(10 pts)**

Problems: Theoretical or Explain in Words

1. Helmholtz energy (A) goes up with increasing pressure at a constant temperature. Now prove it. Hint: $\partial A = -S\,\partial T - P\,\partial V$ **(5 pts)**

2. a. If A is the maximum work out of a system at constant temperature, can a perfect gas with a higher volume perform more work? In other words, $\left.\frac{\partial A}{\partial V}\right)_T$ = ? **(5 pts)**

b. The answer will be overall negative, so why do you think a gas can do less work if it's volume increases at a constant temperature? **(3 pts)**

3. a. Can you show how the Helmholtz energy (A) changes with increasing volume at constant entropy?
Hint: $\left.\frac{\partial T}{\partial V}\right)_S = \frac{-P}{C_V}$. **(5 pts)**

b. At ~room temperature, does A of a gas increase or decrease with increasing volume at constant entropy given that: $\left.\frac{\partial A}{\partial V}\right)_S = P\left(\frac{S}{C_V} - 1\right)$? Hint: Absolute entropies per mol (S_m) of gases vary from ~100→200 J/K/mol at room temperature; how does that compare to typical $C_{V,m}$'s? **(2 pts)**

4. Does Gibbs energy (G) goes up or down with increasing volume at a constant temperature? Hint: $\partial G = -S\,\partial T + V\,\partial P$ **(5 pts)**

5. (Assume we are talking about a perfect gas) To derive the change in G under isothermal conditions ($\partial T = 0$ K) we do the following:

(1) $\partial G = -S\,\partial T + V\,\partial P = V\,\partial P$

Yet if I start with G = H – TS I get the following:

(2) $\partial G = \partial H - T\,\partial S - S\,\partial T = C_P\,\partial T - T\,\partial S - S\,\partial T = -T\,\partial S$ since $\partial T = 0$ K. As it is true that $\partial q_{rev} = -\partial w_{rev}$ at a constant temperature then: $\partial S = \frac{\partial q_{rev}}{T} = -\frac{\partial w_{rev}}{T}$. Insert this into (2) and you get:

(3) $\partial G = -T\,\partial S = \partial w_{rev} = -P\,\partial V$.

Therefore: $-P\,\partial V = V\,\partial P$. This seems very odd! To make sure, let's prove it again another way!

a. If $\partial G = -P\,\partial V$ at constant T, what is $\left.\frac{\partial G}{\partial V}\right)_T = ?$ **(1 pt)**

b. Please simplify the following relationship: $\left.\frac{\partial G}{\partial V}\right)_T \left.\frac{\partial V}{\partial P}\right)_T = \left.\frac{\partial ?}{\partial ?}\right)_?$ **(2 pts)**

c. Show that $\left.\frac{\partial G}{\partial V}\right)_T \left.\frac{\partial V}{\partial P}\right)_T = V$ using $\left.\frac{\partial G}{\partial V}\right)_T = -P$ and $\left.\frac{\partial V}{\partial P}\right)_T$ as determined using the perfect gas equation. **(5 pts)**

d. You have shown that $\left.\frac{\partial G}{\partial V}\right)_T = -P$ and $\left.\frac{\partial G}{\partial P}\right)_T = V$. Can you now show that: $\partial G = -P\,\partial V = V\,\partial P$? **(1 pts)**

6. Can you show that $\left.\frac{\partial U}{\partial P}\right)_T = 0\ \mathrm{J/Pa}$ for a perfect gas? **(7 pts)**

Hint: Start with $\partial U = T\,\partial S - P\,\partial V$. Quickly, you will come to a derivative of entropy; to get rid of it to answer the question, use a Maxwell relation.

7. In the previous question you demonstrated that $\left.\frac{\partial U}{\partial P}\right)_T = 0\ \mathrm{J/Pa}$ for a perfect gas. Now can you show the same for the change in volume, i.e. $\left.\frac{\partial U}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$? Hint: will need a Maxwell relationship. **(7 pts)**

8. We have been assuming that the change in H at a constant T is 0 J; for this problem, do a derivation that proves $\left.\frac{\partial H}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$ for a perfect gas in a closed system. **(7 pts)**

Hint: Start with $\partial H = T\,\partial S + V\,\partial P$. Quickly, you will come to a derivative of entropy; to get rid of it to answer the question, use a Maxwell relation.

9. Now, you should know that: $\left.\frac{\partial H}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$ for a perfect gas, which makes sense as T is constant, however, let's see what happens for a real gas. Can you solve the above for a van der Waals gas that follows the equation of state: $P = \frac{nRT}{V-n\cdot b} - \frac{a\cdot n^2}{V^2}$? **(10 pts)**

10. Is the fact that $\left.\frac{\partial H}{\partial V}\right)_T = \frac{nRT}{V-n\cdot b} - \frac{VnRT}{(V-n\cdot b)^2} + \frac{2a\cdot n^2}{V^2}$ for a real gas consistent with the fact that $\left.\frac{\partial H}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$ for a perfect gas? **(2 pts)**

11. Now, you should know that: $\left.\frac{\partial U}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$ for a perfect gas, which makes sense as T is constant, however, let's see what happens for a real gas. Can you solve: $\left.\frac{\partial U}{\partial V}\right)_T$ for a van der Waals gas that follows the equation of state: $P = \frac{nRT}{V-n\cdot b} - \frac{a\cdot n^2}{V^2}$? **(10 pts)**

12. Is the fact that $\left.\frac{\partial U}{\partial V}\right)_T = \frac{2a\cdot n^2}{V^2}$ for a real gas consistent with the fact that $\left.\frac{\partial U}{\partial V}\right)_T = 0\ \mathrm{J/m^3}$ for a perfect gas? **(2 pts)**

13. Now, you should know that: $\left.\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = 0\ \mathrm{J/m^3}$ for a perfect gas, which makes sense as T is constant. However, let's see what happens for a real gas. Can you solve the above for the Dieterici equation of state is: $\mathrm{P} = \frac{\mathrm{RT}\cdot e^{\frac{-\mathrm{an}}{\mathrm{RTV}}}}{\mathrm{V}-\mathrm{nb}}$?

(10 pts)

14. Does the temperature of a gas increase with increasing pressure at constant entropy (i.e. adiabatic and reversible? Hint: you're looking for $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{S}}$. Start with the fact that $\partial \mathrm{H} = \mathrm{C_P}\,\partial \mathrm{T}$ under adiabatic conditions; note that it is simultaneously true that $\partial \mathrm{H} = \mathrm{V}\,\partial \mathrm{P}$. **(5 pts)**

15. Does the enthalpy (H) of a perfect gas go up or down with increasing volume at constant entropy? Hint: your looking for $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{V}}\right)_{\mathrm{S}}$, and under conditions of constant entropy, the transition must be adiabatic. As such: $\partial \mathrm{H} = \partial \mathrm{U} + \partial(\mathrm{PV})$, and $\partial \mathrm{U} = \mathrm{C_V}\,\partial \mathrm{T}$, and $\left.\frac{\partial \mathrm{T}}{\partial \mathrm{V}}\right)_{\mathrm{S}} = \frac{-\mathrm{P}}{\mathrm{C_V}}$. **(7 pts)**

16. Starting with the Clausius Inequality, $\partial S \geq \frac{\partial \mathrm{q}}{\mathrm{T}}$, can you prove that, under conditions of constant pressure and temperature, for the total entropy to increase, $\partial G < 0\ J$? **(7 pts)**

(Hint, first look in your notes for how we worked the same problem for H at constant S and P, and for A at constant V and T.) **(7 pts)**

17. The Joule-Thomson coefficient is $\mu_{\mathrm{J-T}} = \left.\frac{\partial \mathrm{T}}{\partial \mathrm{P}}\right)_{\mathrm{H}} = -\frac{1}{\mathrm{C_P}}\left.\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{T}}$. Can you solve for $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{T}}$ and show that it is 0 $\mathrm{m^3}$ for a perfect gas? **(7 pts)**

18. Concerning the Joule-Thomson effect, if $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{T}} = \mathrm{V} - \mathrm{T}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$, can you show that for a van der Waals gas that $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{P}}\right)_{\mathrm{T}} \approx \mathrm{nb} - \frac{2\mathrm{na}}{\mathrm{RT}}$? You need to know some approximations, such as $\mathrm{V} \approx \frac{\mathrm{nRT}}{\mathrm{P}} + \mathrm{nb} - \frac{\mathrm{an}}{\mathrm{RT}}$ and $\frac{\mathrm{nR}}{\mathrm{P}} \approx \frac{\mathrm{V}-\mathrm{nb}}{\mathrm{T}} + \frac{\mathrm{na}}{\mathrm{RT^2}}$.

(10 pts)

19. Can you show that $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{S}}\right)_{\mathrm{V}} = \frac{\mathrm{T}}{\mathrm{C_V}}\frac{\alpha}{\kappa_{\mathrm{T}}}$, where $\alpha = \frac{1}{\mathrm{V}}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$ and $\kappa_{\mathrm{T}} = -\frac{1}{\mathrm{V}}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}$? Hint: you will need to use a Maxwell equation and the Euler chain formula in the 1st step. **(10 pts)**

20. Can you $\left.\frac{\partial \mathrm{S}}{\partial \mathrm{P}}\right)_{\mathrm{T}} = -\mathrm{V}\alpha$, where $\alpha = \frac{1}{\mathrm{V}}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}}$ and $\kappa_{\mathrm{T}} = -\frac{1}{\mathrm{V}}\left.\frac{\partial \mathrm{V}}{\partial \mathrm{P}}\right)_{\mathrm{T}}$? Hint: you will need to use a Maxwell equation and the Euler chain formula in the 1st step, and the fact that $\left.\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} = \frac{\alpha}{\kappa_{\mathrm{T}}}$ which was derived in the textbook. **(10 pts)**

Chapter 6: Chemical Thermodynamics: the 3rd Law, Hess's Law, Chemical Potentials, and Reaction Yields

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. We will show how thermodynamics can be used to calculate reaction yields, the freezing temperature of water, and how the boiling point of water is raised 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 chemicals. 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 these heat capacities are not the same. As it isn't easy to keep a solid at a constant volume, we make these measurements at a constant pressure. Recalling that: $\partial \mathrm{q} = \mathrm{C_P}\,\partial \mathrm{T}$, and assuming the heat is added reversibly: $\partial \mathrm{S} = \frac{\partial \mathrm{q_{rev}}}{\mathrm{T}}\big)$, then we see:

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

where $\mathrm{S(0\ K)}$ is 0 J/K due to the 3rd Law. Now you can see how it is the 3rd Law allows us to know what the actual entropy of a chemical is at room temperature and pressure; if we didn't know what $\mathrm{S(0\ K)}$ was, we would never know the absolute value of S at any temperature!

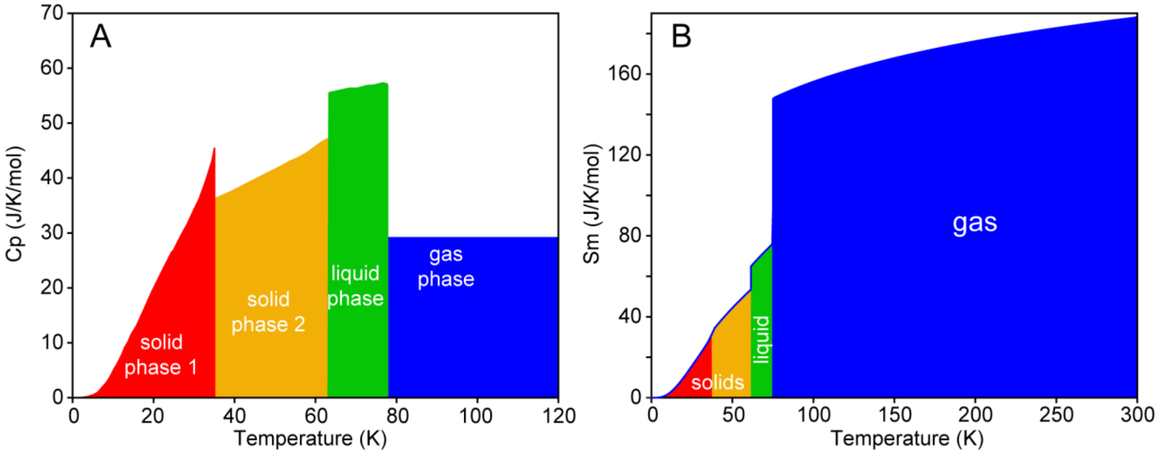


Figure 6.1 A. The heat capacity at constant pressure of N_2 gas reveals several phase transitions including two solid phases. **B.** The integrated heat capacities provide the data to calculate the Entropy per mole of N_2 at standard conditions.

As an example, we will calculate the entropy of nitrogen gas at 25 °C starting from 0 K. First, you may be tempted to use the value of $C_{P,m}$ that we determined in Chapter 2: $C_{P,m} = C_{V,m} + R = \frac{5}{2}R + R = 29.1\ \mathrm{J/K/mol}$. 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 jumps down, 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 ← 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:

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

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 solid 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:

$$S_m = S_m(0\ K) + C_{P,m}(T) \cdot \ln\left(\frac{T_{h\leftarrow c}}{T_i}\right) + \frac{\Delta_{h\leftarrow c}H_m}{T_{h\leftarrow c}} + C_{P,m}(T) \cdot \ln\left(\frac{T_{fus}}{T_{h\leftarrow c}}\right) + \frac{\Delta_{fus}H_m}{T_{fus}} \ldots \qquad (6.1)$$

where “fus” is fusion (the IUPAC word for melting) and T_{fus} is the melting temperature (~64 K). There are additional terms we can add to the entropy summation above 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. When we do this calculation using the $C_{P,m}(T)$ data shown in Figure 6.1A (and phase transformation enthalpies from various publications) 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.

6.1.1 Standard 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, to tabulate thermodynamic data we must stipulate a single temperature at which all the data are valid. If we need to know the thermodynamic data at a different temperature, we can simply take the value at this standard state and then adjust it appropriately. This happens frequently, and we will show how this is done later in this chapter.

Before we get ahead of ourselves, what should we use to define the standard state? How about a standard volume and entropy? There are several reasons not to do so; for example, there is no such thing as an entropy thermometer. Instead, how about we use pressure and temperature? After all, these are intensive variables, and intensive variables are the deciding factors that determine equilibrium (this is explored in Chapter 8). For example, it is not true that water and ice at equilibrium have the same entropy and volume/mol (density), but they do have the same temperature at the same pressure. Thus, we choose room temperature (25 ºC) and pressure (100 kPa, or 1 bar) for the standard state.

6.2 Energy, it’s all relative.

Now that we can calculate and report the entropy per mole of all chemicals at the standard state, we would like to tabulate it with the enthalpy per mole ($H_m = U_m + PV_m$). This will allow us to determine Gibbs energy per mole via $G_m = H_m - T \times S_m$. 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 internal energy per mole U_m as this is the starting point from which all other energetic thermodynamic variables originate.

However, we now run into a terrible problem- we don't have a 3rd 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: $\mathrm{U_m} = \frac{1}{2}\mathrm{RT} \cdot (\text{degrees of freedom})$. 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. This is important because it helped us determine the work done by an expanding piston. What this definition of U ***does not do*** is allow us to determine the energy of the 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 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 σ-bonds of hexane have more or less degrees of freedom of those in the delocalized π-bonds of benzene? And if so, what is the corresponding 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 what we chemists care about anyways.

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 ($\Delta_r H°$, where "r" means reaction and the ° means the value was measured at the standard state). Burning propane is a good example:

$$1\ CH_3CH_2CH_3(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l) \qquad \Delta_r H° = -2219.2\ \text{kJ}$$

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 $\Delta_r H°$'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 energy 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 accurate, this effort will take a huge amount of time and money.

It turns out that we can predict the enthalpies of reactions without actually setting them off; we will demonstrate how this works with some examples such as the combustion of dimethyl ether:

$$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \qquad \Delta_rH° = -1460.4\ kJ$$

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:

$$CH_3CH_2OH(l) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \qquad \Delta_rH° = -1367.0\ kJ$$

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:

$$CH_3OCH_3(g) \rightarrow CH_3CH_2OH(l) \qquad \Delta_rH° = -93.4\ kJ$$

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 sum the combustion reaction of diethyl ether with the reverse reaction of the combustion of ethanol:

$$\begin{array}{c} CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \qquad \Delta_rH° = -1460.4\ kJ \\ + \\ \underline{3\ H_2O(l) + 2\ CO_2(g) \rightarrow CH_3CH_2OH(l)\ + 3\ O_2(g) \qquad \Delta_rH° = 1367.0\ kJ} \end{array}$$

The result is:

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

We put a negative sign in front of the enthalpy of the combustion reaction of ethanol when we wrote the reaction in reverse. Next, there are identical species (oxygen, water, and carbon dioxide) on the right and left of the reaction that can be removed because they don't "do" anything if they are on both sides of the equation. This simplification yields:

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

$$CH_3OCH_3(g) \rightarrow CH_3CH_2OH(l) \qquad \Delta_r H° = -93.4\ \text{kJ}$$

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.

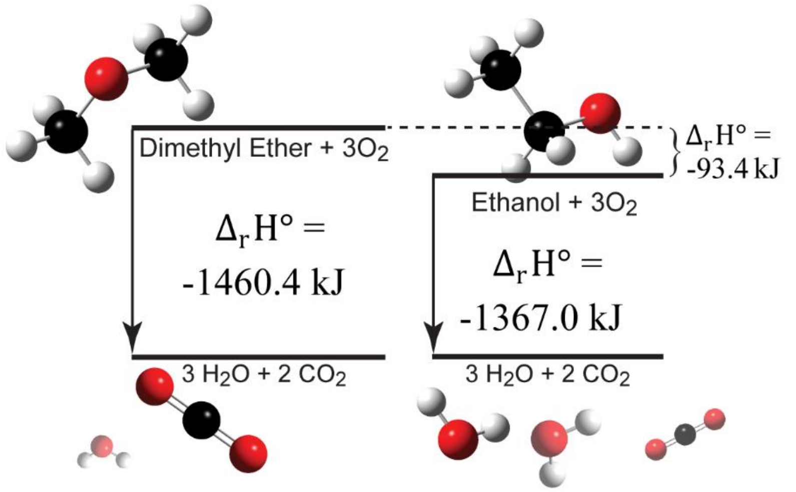


Figure 6.2. The relative heats of combustion of ethanol and dimethyl ether reveal the enthalpy difference between the two organics.

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

$$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O\mathbf{(g)} \qquad \Delta_r H° = -1328.4\ \text{kJ}$$

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

-1328.4 kJ/mol – -1460.4 kJ/mol

= 132.0 kJ/mol

(this is 3× 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

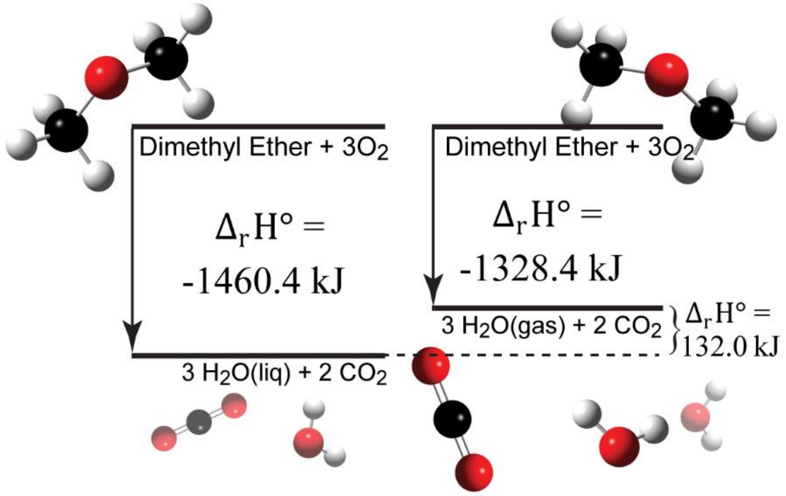


Figure 6.3. The heats of combustion of dimethyl ether reveal the enthalpy difference between liquid water and steam.

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. Let's examine some very generic examples using labels like "A" & "B" etc. for the chemical reactants and products:

$$\begin{array}{cc} \mathrm{A + B \rightarrow C + D} & \Delta_r H^\circ = \mathrm{X\ kJ} \\ + & \\ \underline{\mathrm{C + D \rightarrow F + G}} & \underline{\Delta_r H^\circ = \mathrm{Y\ kJ}} \\ \mathrm{A + B + C + D \rightarrow C + D + F + G} & \Delta_r H^\circ = \mathrm{X + Y\ kJ} \end{array}$$

We simply add the chemicals to the left of the "→" sign together, and ditto for the right side. Likewise we add the enthalpies together. Also, since C and D are on both sides they can be eliminated: $\mathrm{A + B + \cancel{C} + \cancel{D} \rightarrow \cancel{C} + \cancel{D} + F + G}$, leaving:

$$\mathrm{A + B \rightarrow F + G} \qquad \Delta_r H^\circ = \mathrm{X + Y\ kJ}$$

To summarize, we simply add the enthalpies to get the desired result.

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

$$\begin{array}{cc} \mathrm{A + B \rightarrow 2C + 2D} & \Delta_r H^\circ = \mathrm{X\ kJ} \\ + & \\ \mathrm{\tfrac{1}{2}\,F + \tfrac{1}{2}\,G \rightarrow C + D} & \Delta_r H^\circ = \mathrm{Y\ kJ} \end{array}$$

Here, can't directly add these equations together; in fact, we need to reverse the second reaction and then multiply it by 2×. Note that the enthalpy is thus multiplied by -2×, where the minus comes about from reversing the reaction:

$$\begin{array}{cc} \mathrm{2C + 2D \rightarrow F + G} & \Delta_r H^\circ = \mathrm{-2{\times}Y\ kJ} \\ + & \\ \underline{\mathrm{A + B \rightarrow 2C + 2D}} & \underline{\Delta_r H^\circ = \mathrm{X\ kJ}} \\ \mathrm{A + B + 2C + 2D \rightarrow 2C + 2D + F + G} & \Delta_r H^\circ = \mathrm{X - 2{\times}Y\ kJ} \end{array}$$

As in the last example we eliminate the species that appear on both left and right sided to yield:

$$\mathrm{A + B \rightarrow F + G} \qquad \Delta_r H^\circ = \mathrm{X - 2{\times}Y\ kJ}$$

In every example above, the species "C" and "D" were ultimately removed. When we use a basis of reactions whereby the chemicals are formed from elements in their standard states, the "C" and "D" species are those standard state elements.

6.2.2 The standard state. Now concerning our ability to predict the theromochemistry of chemical reactions, we can clearly see that we can form a basis set of data by burning all known chemicals and measuring their heat output. Then, we can simply manipulate the data to form a “gap” between two combustion reactions that is “bridged” by the reaction that we want to know the enthalpy of (this works for Gibbs energy and entropy as well- actually for any state function!). The thermochemistry of this reaction can thus be determined without having to make the experimental measurement! This is a good idea and it would work, except for the fact that not all chemicals can 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, which are the standard pressure and temperature. This isn’t easy for combustion reactions.

So, the idea of a chemical thermodynamic basis set is good, but we just have to pick something other than combustion reactions to form it. 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. For example:

$$2\ \mathrm{C(s,graphite)} + \tfrac{1}{2}\ \mathrm{O_2(g)} + 3\ \mathrm{H_2(g)} \rightarrow \mathrm{CH_3OCH_3(g)} \qquad \Delta_f H_m^\circ = -184.1\ \mathrm{kJ/mol}$$

And for ethanol:

$$2\ \mathrm{C(s,graphite)} + \tfrac{1}{2}\ \mathrm{O_2(g)} + 3\ \mathrm{H_2(g)} \rightarrow \mathrm{CH_3CH_2OH(l)} \qquad \Delta_f H_m^\circ = -277.69\ \mathrm{kJ/mol}$$

Here we see that there are differences with the symbols and units for formation energies. For one, they are per molar quantities since they are defined by the formation for one mole of the chemical species. 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”.

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:

$$\mathrm{CH_3OCH_3(g)} \rightarrow 2\ \mathrm{C(s,graphite)} + \tfrac{1}{2}\ \mathrm{O_2(g)} + 3\ \mathrm{H_2(g)} \qquad -\Delta_f H^\circ = 1\ \mathrm{mol} \times -184.1\ \mathrm{kJ/mol}$$

$$+$$

$$\underline{2\ \mathrm{C(s,graphite)} + \tfrac{1}{2}\ \mathrm{O_2(g)} + 3\ \mathrm{H_2(g)} \rightarrow \mathrm{CH_3CH_2OH(l)} \qquad \Delta_f H^\circ = 1\ \mathrm{mol} \times -277.69\ \mathrm{kJ/mol}}$$

$$\mathrm{CH_3OCH_3(g)}+2\mathrm{C(s,graphite)}+\tfrac{1}{2}\mathrm{O_2(g)}+3\mathrm{H_2(g)} \rightarrow \mathrm{CH_3CH_2OH(l)}+2\mathrm{C(s,graphite)}+\tfrac{1}{2}\mathrm{O_2(g)}+3\mathrm{H_2(g)}$$

After removing the redundant species on both sides of the equation we are left with:

$CH_3OCH_3(g) \rightarrow CH_3CH_2OH(l)$ 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 did have 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 calculating the same from the combustion data (-93.4 kJ from page 107); this is common, and results from experimental errors, the source of your data, and rounding errors.

Before we work some more examples we must tabulate formation thermodynamic data such as that in Table 6.1. 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	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

Table 6.1. Standard thermochemical data for selected compounds.

Here we can see that the Gibbs energy and enthalpy of $O_2(g)$ 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. Of course, they still have 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. With the data in Table 6.1 we can calculate the thermochemistry of combustion of dimethyl ether.

6.3 Enthalpy and Gibbs Energy of Formation: Hess's Law examples.

Given that we now accept 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:

$$CH_3OCH_3(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(l) \qquad \Delta_c H° = -1460.4\ kJ$$

The reaction enthalpy is determined from:

$$\Delta_r H° = \sum_{\text{products}} \upsilon \cdot \Delta_f H_m^{\circ} - \sum_{\text{reactants}} \upsilon \cdot \Delta_f H_m^{\circ} \tag{6.2}$$

Likewise:

$$\Delta_r G° = \sum_{\text{products}} \upsilon \cdot \Delta_f G_m^{\circ} - \sum_{\text{reactants}} \upsilon \cdot \Delta_f G_m^{\circ}$$

$$= \sum_{\text{products}} \upsilon \cdot (\Delta_f H_m^{\circ} - T\Delta_f S_m^{\circ}) - \sum_{\text{reactants}} \upsilon \cdot (\Delta_f H_m^{\circ} - T\Delta_f S_m^{\circ}) \tag{6.3}$$

where υ is the stoichiometric number of moles that each species contributes to the reaction and the symbol ^{o} means that the data are measured under standard conditions (25 °C and 1 bar pressure). These equations are Hess's Law, which is really a manifestation of the 1st 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:

$$\Delta_r H° = \sum_{\text{products}} \upsilon \cdot \Delta_f H_m^{\circ} - \sum_{\text{reactants}} \upsilon \cdot \Delta_f H_m^{\circ}$$

$$= 3\ \text{mol} \times -285.83\frac{\text{kJ}}{\text{mol}} + 2\ \text{mol} \times -393.509\frac{\text{kJ}}{\text{mol}} - 3\text{mol} \times 0.0\frac{\text{kJ}}{\text{mol}}$$

$$- 1\ \text{mol} \times 184.1\frac{\text{kJ}}{\text{mol}} = -1460.4\ \text{kJ/mol}$$

and:

$$\Delta_r G° = \sum_{\text{products}} \upsilon \cdot \Delta_f G_m^{\circ} - \sum_{\text{reactants}} \upsilon \cdot \Delta_f G_m^{\circ}$$

$$= 3\ \text{mol} \times -237.129\frac{\text{kJ}}{\text{mol}} + 2\ \text{mol} \times -394.359\frac{\text{kJ}}{\text{mol}} - 3\text{mol} \times 0.0\frac{\text{kJ}}{\text{mol}}$$

$$- 1\ \text{mol} \times 135.2\frac{\text{kJ}}{\text{mol}} = -1364.9\ \text{kJ/mol}$$

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

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

For example, take the thermochemical data on dimethyl ether:

Material	S_m° (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 $\Delta_f G_m^\circ$ from $\Delta_f H_m^\circ$ = -184.1 kJ/mol and S_m° = 342.2 J/K/mol, which is:

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

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

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

which is:

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

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 $\Delta_f S_m^\circ = -164.09\ \text{J/K/mol}$. When we use entropy properly we see that the data table is self-consistent:

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

Consequently, our understanding of how Gibbs energy is related to enthalpy and entropy is solid, but of course we don't recommend going through all of these calculations if a table of $\Delta_f G_m^\circ$'s is available. However, when we calculated $\Delta_f G_m^\circ$ above using $\Delta_f H_m^\circ - T^\circ \times \Delta_f S_m^\circ$, what if we used a different temperature other than T°=25 °C (the standard state temperature)?

6.3.1 Non-standard state reactions and Kirchoff's Law. The example above gives us an idea how to determine if a reaction is spontaneous at different temperatures. This is important because we know that not all chemical reactions will occur at exactly 1 bar pressure and 25 ºC, i.e. they are not spontaneous because $\Delta_r G° > 0\,J$, which also means that total entropy does not increase as required by the 2nd Law. Our intuition also tells us that heating a chemical reaction will often make it "go", i.e. become spontaneous because $\Delta_r G < 0\,J$. As a result, we often must adjust our thermochemical data for conditions other than the standard state. Here we will focus on temperature. We already discussed how enthalpy changes with temperature in Ch. 3:

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

Integration yields $\Delta H = C_P \Delta T$. This is incomplete though, since we need to apply lower and upper 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 this some unspecified T_2. Let's not forget that we need to do everything on a per molar basis as well. Thus:

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

likewise:

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

assuming that the heat capacity is not temperature dependent which is not fully correct (we will make that simplification regardless). To summarize, to determine enthalpy at temperatures other than 25 ºC, we determine the change in enthalpy of each species at the new temperature:

$$\Delta_f H_m(T_2) = \Delta_f H_m^{\circ}(298.15K) + C_{P,m}^{\circ} \times (T_2 - 298.15K)$$

and then perform a standard Hess's Law calculation, i.e.:

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

Recall that our goal is to determine the change in Gibbs Energy, and for this we now 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 for the standard state temperature as:

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

Example Problem 6.1

Problem: The dissociation of water: $H_2O_{(g)} \rightarrow H_{2(g)} + \frac{1}{2} O_{2(g)}$ is has a very high $\Delta_r G^\circ = +228.57$ kJ under standard conditions. Is the same true at 4000 K?

Answer: First, let us calculate:

$\Delta_r C_P^\circ = \sum_{\text{products}} \upsilon \cdot C_{P,m}^\circ - \sum_{\text{reactants}} \upsilon \cdot C_{P,m}^\circ = 0.5 \text{ mol} \times 29.41 \frac{\text{J}}{\text{K}\cdot\text{mol}} + 1.0 \text{ mol} \times 28.64 \frac{\text{J}}{\text{K}\cdot\text{mol}} - 1 \text{ mol} \times 33.58 \frac{\text{J}}{\text{K}\cdot\text{mol}} = 9.765 \frac{\text{J}}{\text{K}}$

$\Delta_r H^\circ = \sum_{\text{products}} \upsilon \cdot \Delta_f H_m^\circ - \sum_{\text{reactants}} \upsilon \cdot \Delta_f H_m^\circ = 0.5 \text{ mol} \times 0 \frac{\text{kJ}}{\text{mol}} + 1.0 \text{ mol} \times 0 \frac{\text{kJ}}{\text{mol}} - 1 \text{ mol} \times -241.818 \frac{\text{kJ}}{\text{mol}} = 241.818 \text{ kJ}$

$\Delta_r S^\circ = \sum_{\text{products}} \upsilon \cdot S_m^\circ - \sum_{\text{reactants}} \upsilon \cdot S_m^\circ = 0.5 \text{ mol} \times 205.138 \frac{\text{J}}{\text{K}\cdot\text{mol}} + 1.0 \text{ mol} \times 130.684 \frac{\text{J}}{\text{K}\cdot\text{mol}} - 1 \text{ mol} \times 188.825 \frac{\text{J}}{\text{K}\cdot\text{mol}} = 44.428 \frac{\text{J}}{\text{K}}$

Next, we plug this into the formula described on page 114:

$\Delta_r H(T_2) = \Delta_r H^\circ(298.15\text{K}) + \Delta_r C_P^\circ \times (4000\text{K} - 298.15\text{K}) = 278.0$ kJ

$\Delta_r S(T_2) = \Delta_r S_m^\circ(298.15\text{K}) + \Delta_r C_P^\circ \times \ln\left(\frac{4000\text{K}}{298.15\text{K}}\right) = 69.782 \frac{\text{J}}{\text{K}}$

Last, $\Delta_r G(T_2) = \Delta_r H(T_2) - 4000\text{K} \times \Delta_r S(T_2) = -1.16$ kJ, which clearly demonstrates that the reaction can be made spontaneous, albeit at a much higher temperature than 298.15 °C!

To verify your understanding, try this calculation at 2000 K, where you should find that $\Delta_r G(2000 \text{ K}) = +132.41$ kJ.

With the knowledge of the proper entropy change of every chemical species in the reaction, the net entropy change is thus: $\Delta_r S = \sum_{\text{products}} \upsilon \cdot S_m(T_2) - \sum_{\text{reactants}} \upsilon \cdot S_m(T_2)$. 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:

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

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

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

Likewise, the change in the reaction entropy at T_2:

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

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 exhaustively demonstrated that we have to increase the temperature to lower $\Delta_r G$. Could we have known that before going through those tortuous exercises of calculator work? The answer is yes via the Gibbs-Helmholtz equation:

$$\left.\frac{\partial\left({}^{\Delta_r G}/_{T}\right)}{\partial T}\right)_P = -\frac{\Delta_r H}{T^2} \tag{6.4}$$

From this we can immediately see that, if $\Delta_r H$ is positive (the reaction is endothermic), then the derivative $\left.\frac{\partial({}^{\Delta G}/_{T})}{\partial T}\right)_P$ is negative. Thus, if ∂T of the left is positive (temperature increases) then $\partial(\Delta G/T)$ is negative. This means that ΔG decreases, since there is no such thing as a negative T. To symmarize, ΔG decreases with increasing temperature for endothermic reactions. We can make this clearer if we integrate the Gibbs-Helmholtz equation $\partial\left({}^{\Delta G}/_{T}\right) = -\frac{\Delta_r H°}{T^2}\partial T$ as shown here:

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

We assume that the lower limit is the standard state temperature. It is difficult to see it, but the quantity we are trying to calculate, $\Delta_r G(T_2)$, is in the upper limit of the left-hand integral. Solving yields:

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

Example Problem 6.2

Problem. The way we create hydrogen gas is from steam reforming, which is: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\ H_2(g)$ (note: we get hydrogen from gasoline, essentially). However, the reaction is not spontaneous: $\Delta_r G° = -137.168\,\frac{kJ}{mol} + 3mol \times 0\,\frac{kJ}{mol} - -50.72\,\frac{kJ}{mol} - -228.572\,\frac{kJ}{mol} = 142.124\ kJ$

Or, we should say not spontaneous at the standard temperature and pressure. What temperature will the reaction become spontaneous, i.e. when is $\Delta_r G(T_2) = 0$ kJ? We will assume that the heat capacities are temperature independent.

Answer: We have already found that the reaction is not spontaneous. Thus, we need to collect the enthalpy, entropy and heat capacity "pieces" and assemble them together to the Gibbs energy at an alternate T_2 that is not the standard temperature such that $\Delta_r G(T_2) = 0$ kJ. First we calculate the change in enthalpy of the reaction via:

$\Delta_r H°(298.15K) = \sum_{products} \upsilon \cdot \Delta_f H_m^{\circ} - \sum_{reactants} \upsilon \cdot \Delta_f H_m^{\circ}$ =1 mol×-110.5 kJ/mol + 3 mol×0 kJ/mol – 1 mol×-241.8 kJ/mol – 1 mol×-74.8 kJ/mol = 206.1 kJ.

Note that since this reaction is endothermic, we will have to increase the temperature to decrease $\Delta_r G$. Also, the change in entropy is:

$\Delta_r S°(298.15K) = \sum_{products} \upsilon \cdot S_m^{\circ} - \sum_{reactants} \upsilon \cdot S_m^{\circ}$ = 1 mol×197.7 J/K/mol + 3 mol×130.7 J/K/mol – 1 mol×188.8 J/K/mol – 1 mol×186.3 J/K/mol = 214.7 J/K. Note that positive change in entropy results from the creation of 4 moles of product gas from 2 moles of reactants. The change in the reaction heat capacity is likewise:

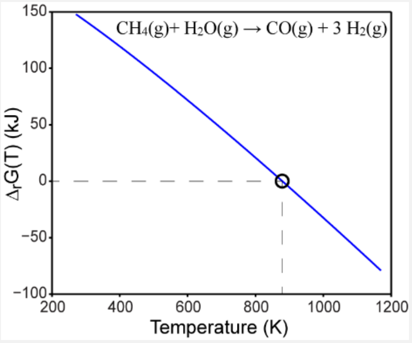
$\Delta_r C_P^{\circ}(298.15K) = \sum_{products} \upsilon \cdot C_{P,m}^{\circ} - \sum_{reactants} \upsilon \cdot C_{P,m}^{\circ}$ = 1 mol×29.14 J/K/mol + 3 mol×28.82 J/K/mol – 1 mol×33.58 J/K/mol – 1 mol×35.31 J/K/mol = 46.71 J/K.

Applying Kirchoff's Law yields: $\Delta_r G(T_2) = \Delta_r H(T_2) - T_2 \times \Delta_r S(T_2) =$

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

$$= 206.1\ kJ\ + 0.04671\ kJ/K \times (T_2 - 298.15K) - T_2 \times \left(0.2147\ kJ/K + 0.04671\ kJ/K \times \ln\left(\frac{T_2}{298.15K}\right)\right)$$

Simplification gives us: $\Delta_r G(T_2) = 192.173\ kJ + T_2 \times 0.09814\ kJ/K - T_2 \times 0.04671\ kJ/K \times \ln(T_2)$. Now you must graph the equation to find where $\Delta_r G(T_2) = 0$ kJ as shown here. Examination demonstrates that the reaction becomes spontaneous above 879.43 K = 606.3 ºC.



This 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, we find that $\Delta_r G(T_2) = 0$ 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 simplify the equation for $\Delta_r G(T_2)$ as shown here:

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

and since $\Delta_r G° = \Delta_r H° - 298.15K \times \Delta_r S°$ then we can show that:

$$\Delta_r G(T_2) = \Delta_r H° - T_2 \times \Delta_r S°$$

So, the result is rather trivial; we simply used the equation for the standard state Gibbs energy: $\Delta_r G° = \Delta_r H° - T° \times \Delta_r S°$, where T° = 298.15 K, and inserted a non-standard temperature T_2. While solving this equation 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 the result of the derivation 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 $\int_{T_1=298.15\ K}^{T_2} \frac{-\Delta_r H°}{T^2} \partial T$ 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:

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

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 $\Delta_r G°$ 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:

$$\int_{\sum_{\text{reactants}} \upsilon \cdot \Delta_f G_m^\circ}^{\sum_{\text{products}} \upsilon \cdot \Delta_f G_m^\circ} \partial(\Delta_r G) = \sum_{\text{products}} \upsilon \cdot \Delta_f G_m^\circ - \sum_{\text{reactants}} \upsilon \cdot \Delta_f G_m^\circ = \Delta_r G^\circ$$

This is depicted graphically in Figure 6.4A. If $\Delta_r G^\circ < 0\,J$ then a reaction will go to completion as the most total entropy is generated in the process. Otherwise, there is no reaction at all since the Universe will have less entropy as a result; the 2nd Law forbids this.

Does this make sense? Afterall, most synthetic chemists report finite reaction yields, and work hard to optimize them. Yet the analysis above stipulates that reaction yields are either 0% or 100%. 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 $\epsilon = 0$ (all reactants) to $\epsilon = 1$ (all products). As shown in Figure 6.4B, if there is a minimum in the Gibbs energy below either product or reactant at point $\epsilon = \alpha$, then the reaction will stop there as this is where most total entropy is generated. We can calculate the reaction yield from point α.

In this section we will use chemical thermodynamics to determine the yield of a reaction. What we do know is that when the reaction stops, it must be true that $\Delta_r G = \frac{\partial G}{\partial \epsilon} = 0$ J. This is because the change in Gibbs energy tells us how the total entropy is increasing, so long as temperature and pressure are held constant. Thus, if the reaction progressing results in no change in Gibbs energy, then the reaction stops and the system is at equilibrium. Clearly, we need to know the mechanism by which $\Delta_r G$ changes as a spontaneous reaction proceeds from initiation. This will also allow us to calculate the reaction yield. As usual, we will start with a simple example.

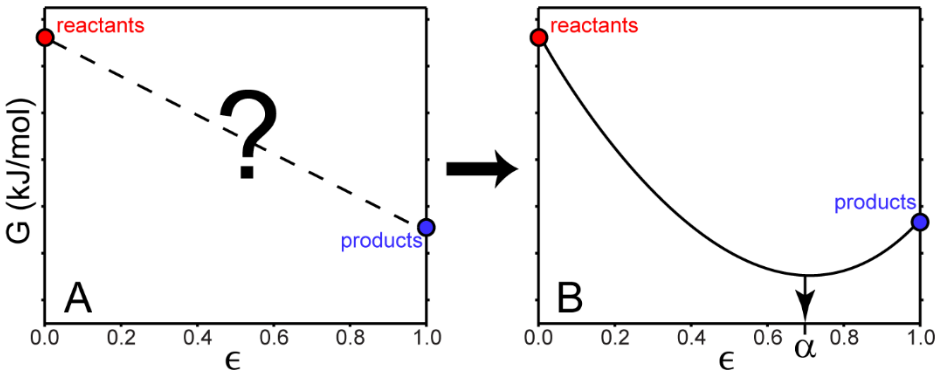


Figure 6.4. A. Without consideration of the Gibbs energy as a function of the extent of reaction (ϵ), we assume that the result is either all products or no reaction. **B.** However, a minimum in Gibbs energy can exist that defines the optimum (α) extent of reaction.

6.4.1 Phase Changes. We will start analyzing chemical reactions using the example of ice melting. Although it is boring, it has the benefit of being very simple to analyze. First, we need to realize that the 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, which is true of reactants and products, respectively.

In our previous derivations of U, H, A and G we never considered that the moles of gas 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:

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

Likewise:

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

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

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

This is all rather unfortunate, because it appears that all of our energy equations just became even more complicated! But, is that so? For example, we know that $\mathrm{H} = \mathrm{U} + \mathrm{PV}$, which of course leads to:

$$\partial \mathrm{H} = \partial \mathrm{U} + \partial(\mathrm{PV})$$

Now we substitute in the above:

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

which can be simplified as:

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

After doing some cancellation and taking like terms to one side:

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

which means that $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{n}}\right)_{\mathrm{P,S}} \partial \mathrm{n} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{n}}\right)_{\mathrm{V,S}} \partial \mathrm{n}$; division by $\partial \mathrm{n}$ leads to $\left.\frac{\partial \mathrm{H}}{\partial \mathrm{n}}\right)_{\mathrm{P,S}} = \left.\frac{\partial \mathrm{U}}{\partial \mathrm{n}}\right)_{\mathrm{V,S}}$. Similar derivations reveal that:

$$\left.\frac{\partial G}{\partial n}\right)_{P,T} = \left.\frac{\partial A}{\partial n}\right)_{V,T} = \left.\frac{\partial H}{\partial n}\right)_{P,S} = \left.\frac{\partial U}{\partial n}\right)_{V,S} \qquad (6.5)$$

It appears that, however we express the change in energy per mole and whatever conditions are held constant, we are dealing with the same quantity which we call the chemical potential (μ). Thus, the change in energy with increasing / decreasing moles of a chemical substance in a system can be expressed 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 chemical reaction. And here that reaction will be the melting of an ice cube into liquid water, which are characterized by their chemical potentials μ_{ice} and μ_{water}, respectively. 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:

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

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 $\partial n_{\text{ice}} = -\partial n_{\text{water}}$, which we can insert into the above as: $\mu_{\text{water}}\,\partial n_{\text{water}} - \mu_{\text{ice}}\,\partial n_{\text{water}} = 0\text{ J}$, which can be rearranged as:

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

Since it is possible to have microscopic mass transfer even at equilibrium ($\partial n_{\text{water}} > 0\text{ mol}$), it must be true that $\mu_{\text{water}} - \mu_{\text{ice}} = 0\text{ J/mol}$, and thus $\mu_{\text{water}} = \mu_{\text{ice}}$ at equilibrium. We just proved that the chemical potentials of things at equilibrium are equal!

Now let’s do something more interesting, like raising 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 (of course at constant T and P). This requires a negative change in Gibbs energy:

$$\Delta_r G = \mu_{\text{water}}\Delta n_{\text{water}} + \mu_{\text{ice}}\Delta n_{\text{ice}} < 0\,J$$

which trickles down to $(\mu_{\text{water}} - \mu_{\text{ice}})\Delta n_{\text{water}} < 0\,J$ for the same reasons as above. Now since $\Delta n_{\text{water}} > 0\,mol$ because the ice is melting, then it must be true that $\mu_{\text{water}} - \mu_{\text{ice}} < 0\,J/mol$, requiring $\mu_{\text{water}} < \mu_{\text{ice}}$. 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 the net change is $\Delta_r\mu = 0\ \mathrm{J/mol}$. 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. As the reaction progresses, its chemical potential changes- but how? Here is a simple observation- as the reactant is consumed in the reaction, its partial pressure decreases. This is akin to performing work (see Sec. 2.2):

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

From here we insert the perfect gas relationship to modify the equation for pressure:

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

where we will assume that the initial pressure P_i is the standard state pressure P° = 1 bar (recall that the ° symbol refers to the standard state, 298.15 K and 1 bar pressure). This work changes the energy per mole as: $\frac{\Delta w}{n} = RT \cdot \ln\left(\frac{P_f}{P^\circ}\right)$, and can be added to the initial energy per mole (μ°) to represent the chemical potential of the reactant as it is depleted while forming the product:

$$\mu = \mu^\circ + RT \cdot \ln\left(\frac{P_f}{P^\circ}\right) \tag{6.5}$$

Now we can make another modification to the above, which is to use Dalton's Law which states that the final pressure P_f 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:

$$\mu = \mu^\circ + RT \cdot \ln\left(\frac{\chi \cdot P}{P^\circ}\right) \tag{6.6}$$

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

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

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

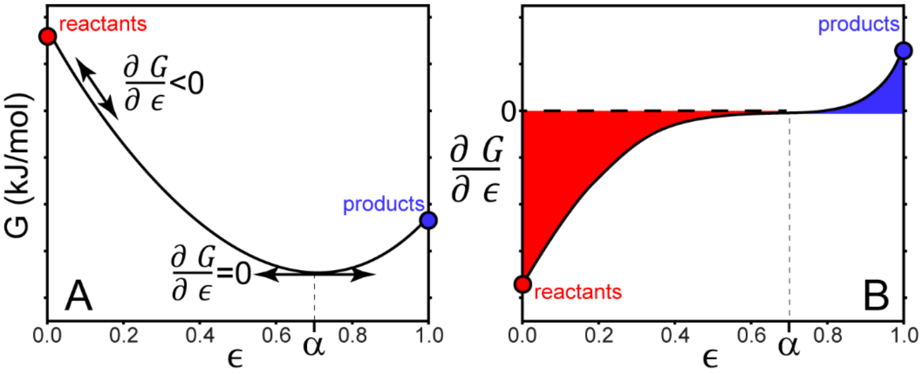


Figure 6.5. A. G vs. ϵ demonstrate how the derivative of the Gibbs energy with the extent of the reaction defines equilibrium at point α. **B.** Integration of the derivative shows how to determine the most negative $\Delta_r G$ possible.

where we used the definition of chemical potential $\left.\frac{\partial G}{\partial n}\right)_i = \mu_i$ and inserted an index "i" to delineate the various chemical participants (e.g. the reactants and products). We will now analyze the energies further using the extent of the reaction "ϵ" that we introduced at the beginning of this section. Recall that ϵ varies from $0 \rightarrow 1$, where $\epsilon = 0$ represents the initial reactant state and $\epsilon = 1$ is for all products. 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? First, we assume that $\partial\epsilon$ is positive (the reaction goes forward). 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 $\Delta_r G$ is realized, which is also where the most total entropy is generated. We can see this more clearly if we plot the derivative $\frac{\partial G}{\partial \epsilon}$ vs. ϵ as in Figure 6.5 B, and note that:

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

The area under the curve starting from the reactant side to point $\epsilon = \alpha$ (red shaded area) generates the most negative net $\Delta_r G$ possible. Further progression of the reaction diminishes the net $\Delta_r G$ as the additional energy contribution is positive (blue shaded area), which consumes 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: $\partial\mathrm{n} = \upsilon \cdot \partial\epsilon$, where υ represents the stoichiometric coefficient of a reactant or product. As such, υ is positive for products, because these "appear" during the reaction, while υ is negative for reactants since they "disappear". We insert these ideas into the change of Gibbs energy:

$$\partial\mathrm{G} = \sum \mu_\mathrm{i} \cdot \partial\mathrm{n} = \sum_{\mathrm{products}} \upsilon_\mathrm{i} \cdot \mu_\mathrm{i} \cdot \partial\epsilon - \sum_{\mathrm{reactants}} \upsilon_\mathrm{i} \cdot \mu_\mathrm{i} \cdot \partial\epsilon$$

$$= \left(\sum_{\mathrm{products}} \upsilon_\mathrm{i} \cdot \mu_\mathrm{i} - \sum_{\mathrm{reactants}} \upsilon_\mathrm{i} \cdot \mu_\mathrm{i} \right) \cdot \partial\epsilon$$

As a result, we can now conclude that:

$$\frac{\partial\mathrm{G}}{\partial\epsilon} = \sum_{\mathrm{products}} \upsilon_\mathrm{i} \cdot \mu_\mathrm{i} - \sum_{\mathrm{reactants}} \upsilon_\mathrm{i} \cdot \mu_\mathrm{i}$$

Using the above relationship with the mole fraction (χ)-dependent chemical potentials $\mu_\mathrm{i} = \mu_\mathrm{i}^{\circ} + \mathrm{RT} \cdot \ln\left(\frac{\chi \cdot \mathrm{P_i}}{\mathrm{P}^\circ}\right)$ allow us to find the composition of a reactive system when the reaction reaches equilibrium (where $\frac{\partial\mathrm{G}}{\partial\epsilon} = 0\ \mathrm{J}$). 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: $\mu = \frac{\partial\mathrm{G}}{\partial\mathrm{n}} = \frac{\mathrm{G}}{\mathrm{n}} = \mathrm{G_m}$, which is true because energy and moles are extensive quantities and can be integrated as:

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

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. $\mu^\circ = \mathrm{G}_\mathrm{m}^{\circ} = \Delta_\mathrm{f}\mathrm{G}_\mathrm{m}^{\circ}$. When we put this all together, we see that $\mu = \mu^\circ + \mathrm{RT} \cdot \ln\left(\frac{\chi \cdot \mathrm{P}}{\mathrm{P}^\circ}\right)$ is equivalent to $\Delta_\mathrm{f}\mathrm{G_m} = \Delta_\mathrm{f}\mathrm{G}_\mathrm{m}^{\circ} + \mathrm{RT} \cdot \ln\left(\frac{\chi \cdot \mathrm{P}}{\mathrm{P}^\circ}\right)$. This also means that $\frac{\partial\mathrm{G}}{\partial\epsilon}$ is the "instantaneous" $\Delta_\mathrm{r}\mathrm{G}$ at point ϵ along the reaction.

At this point you may be overwhelmed with the complexity of composition-dependent chemical potentials during a reaction; this will hopefully be clarified by several examples. First, we will start with something simple:

$$A(g) \rightarrow B(g)$$

for determining the reaction yield. Each species has its own $\Delta_f G_m^\circ$. Starting with $\Delta_r G$:

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

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

These identities are useful: $y \cdot \ln(x) = \ln(x^y)$; $\ln(x) - \ln(y) = \ln(x \cdot y^{-1})$; and $x^A \cdot x^{-B} = x^{A-B}$:

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

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

Given the example above there is a 1:1 stoichiometry of A and B, and thus the stoichiometric coefficients ($\nu_{A,B}$) are equal to 1 mol. This allows us to simplify: $\left(\frac{P}{P^\circ}\right)^{\nu_B - \nu_A} = \left(\frac{P}{P^\circ}\right)^0 = 1$. 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:

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

Now we ask ourselves, 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 the reaction yield, i.e. χ_B and χ_A at equilibrium. And at the end of a reaction $\Delta_r G = \nu_B \cdot \mu_B - \nu_A \cdot \mu_A = 0\ J$, 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:

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

Note that $\Delta_f G^\circ_{B,m} - \Delta_f G^\circ_{A,m} = \Delta_r G^\circ$ 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 (in this example).

Now 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 $\chi_A + \chi_B = 1$. Before we go further, 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 of A and n·α number moles of B at the end of the reaction:

	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. 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:

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

With a numerical value for $\Delta_r G^\circ$ from a Hess's Law calculation, we can thus determine α which is basically 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:

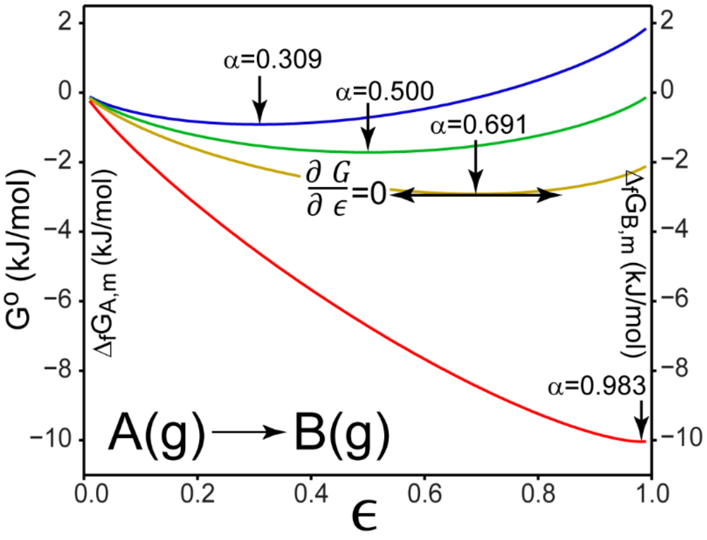


Figure 6.5. G vs. ϵ demonstrate that various $\Delta_r G^o$ (+2 kJ/mol, 0 kJ/mol, -2 kJ/mol and -10 kJ/mol) govern the extent of the reaction.

Example Problem 6.3

Problem: At equilibrium: $A_{(g)} \leftrightarrow 2\ B_{(g)}$ and has a $\Delta_r G°$ = 0 J from a Hess's Law calculation. What is $\Delta_r G$, the extent of the reaction, and the equilibrium constant K at equilibrium if T = 25 °C and the pressure is maintained at P = 1 bar?

Answer: First, at equilibrium $\Delta_r G$ = 0 J by definition. Now we calculate K from:

$$\Delta_r G = \Delta_r G° + RT \cdot \ln(K)$$

where all the G's are 0 J: 0 J = 0 J + RT·ln(K). This is only true if K = 1 (note how the constant has no units). Now for the extent of the reaction: First make a table according to the reaction as so:

	A	**B**
Initial	n	0
Equilibrium	$n - n\alpha$	$2n\alpha$
Mole fractions	$\frac{1-\alpha}{1+\alpha}$	$\frac{2\alpha}{1+\alpha}$
Partial pressures	$\frac{1-\alpha}{1+\alpha}P$	$\frac{2\alpha}{1+\alpha}P$

where α (the extent of the reaction) represents the loss of A. The total number of moles is $n–n\cdot\alpha + 2\alpha\cdot n = n + n\cdot\alpha$. This makes the mole fraction for A: $\chi_A = \frac{(1-\alpha)\cdot n}{(1+\alpha)\cdot n} = \frac{1-\alpha}{1+\alpha}$; the mole fraction of B is found in a similar manner. The partial pressures are then the mole fractions times the total pressure P. Now at equilibrium $K = \prod_i \left(\frac{P_i}{P°}\right)^{\nu_i}$ where P_i is the partial pressure of species i. The equilibrium constant is now: $K = \frac{\left(\frac{2\alpha}{1+\alpha}\cdot\frac{P}{P°}\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\cdot\frac{P}{P°}\right)}$. Simplification yields: $K = \left(\frac{2\alpha}{1+\alpha}\cdot\frac{P}{P°}\right)^2\left(\frac{1+\alpha}{1-\alpha}\cdot\frac{P}{P°}\right) = \frac{4\alpha^2}{(1+\alpha)(1-\alpha)}\cdot\frac{P}{P°}$. As P° = 1 bar and since the total pressure is also 1 bar, all the pressures disappear: $K = \frac{4\alpha^2}{(1+\alpha)(1-\alpha)} = \frac{4\alpha^2}{1-\alpha^2}$. Now since K=1, all we have to do is solve for α: $1 = \frac{4\alpha^2}{1-\alpha^2}$, which is α = 0.447 or 44.7%.

A good question to ask is why does a $\Delta_r G°$ = 0 J reaction A→2B dissociate less than A→B? Given that these are entirely entropically driven reaction yields, in the former case (A→2B) the A molecule doesn't need to dissociate as much to have more B mixing partners compared to the latter example.

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

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 to completion! This is graphically illustrated in Figure 6.5, along with the scenario of $\Delta_r G° \geq 0\ \mathrm{J}$, $\Delta_r G° \leq 0\ \mathrm{J}$, and finally $\Delta_r G° \ll 0\ \mathrm{J}$. The way that the $\mathrm{G\ vs.}\ \epsilon$ curve bends downwards is due to the entropy of mixing between the product and reactant as discussed below.

6.4.3 Entropic Contribution. In the example above, you get a product yield of 50% even though the Hess's Law calculation has $\Delta_r G° = 0\ \mathrm{J}$. Why do we get any products from a formally non-spontaneous reaction? The answer lies in the fact that changes in Gibbs energy is derived from enthalpy and entropy. It turns out that entropy can drive a reaction forward even when it is not spontaneous. To understand, recall that at constant temperature the change in a system entropy per mole is: $\Delta S_m = -\mathrm{R} \cdot \ln\left(\frac{P_f}{P_i}\right)$, which when multiplied by -T gives us:

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

which is the same composition-adjustment factor that was applied to the chemical potential: $\mu = \mu° + \mathrm{RT} \cdot \ln\left(\frac{\chi \cdot P}{P°}\right)$ (note that $P_i = P° = 1\ \mathrm{bar}$ and $P_f = \chi \cdot P$). 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 $\mathrm{G\ vs.}\ \epsilon$ curves in Figure 6.5 bow downwards near the middle of the graph, where mixing is greatest. More products form in the case of $\Delta_r G°$ = -10 kJ, however, which is due to the generation of greater total entropy by a near-100% reaction yield. One way this could be realized is if the reaction generates a lot of heat (i.e. has a large negative enthalpy). In this situation, the entropy created exterior to the system by the shedding of heat overshadows the entropic effects of mixing in the system; this will favor generating products.

6.5 Equilibrium Constants.

Let's derive more generic expressions for the thermochemistry of real chemical reactions with arbitrary numbers of reactants and products; a few example problems are provided following. In general:

Example Problem 6.4

Problem: At 1 bar of pressure and at 2000 K, water has dissociated by 0.6215% at equilibrium via: $2\ H_2O_{(g)} \leftrightarrow 2\ H_{2(g)} + O_{2(g)}$. What are K, $\Delta_r G$, and $\Delta_r G°$?

Answer: First, at equilibrium $\Delta_r G = 0$ J by definition (this was a trick question). Now we will calculate K and then $\Delta_r G°$; we will do so by using a table to express changes in moles:

	H_2O	**H_2**	**O_2**
Initial	2n	0	0
Equilibrium	2n–2n·α	2n·α	n·α
Mole fractions	$\frac{2-2\alpha}{2+\alpha}$	$\frac{2\alpha}{2+\alpha}$	$\frac{\alpha}{2+\alpha}$
Partial pressures	$\frac{2-2\alpha}{2+\alpha}P$	$\frac{2\alpha}{2+\alpha}P$	$\frac{\alpha}{2+\alpha}P$

where α represents the fractional loss of the reactant water. The total number of moles is 2n–2n·α + 2n·α + n·α = 2n + n·α. This makes the mole fraction for water $\chi_{H_2O} = \frac{2n-2n\alpha}{2n+n\alpha} = \frac{2-2\alpha}{2+\alpha}$; the other mole fractions are found in a similar manner. The partial pressures are then the mole fractions times the total pressure P. At equilibrium $K = \prod_i \left(\frac{P_i}{P°}\right)^{\nu_i}$ where P_i is the partial pressure of species i:

$$K = \frac{\left(\frac{2\alpha}{2+\alpha}\cdot\frac{P}{P°}\right)^2\left(\frac{\alpha}{2+\alpha}\cdot\frac{P}{P°}\right)}{\left(\frac{2-2\alpha}{2+\alpha}\cdot\frac{P}{P°}\right)^2}$$

Simplification gives:

$K=\left(\frac{2\alpha}{2+\alpha}\cdot\frac{P}{P°}\right)^2\left(\frac{\alpha}{2+\alpha}\cdot\frac{P}{P°}\right)\left(\frac{2+\alpha}{2-2\alpha}\cdot\frac{P°}{P}\right)^2 = \frac{4\alpha^3}{(2+\alpha)^3}\frac{(2+\alpha)^2}{(2-2\alpha)^2}\left(\frac{P}{P°}\right) = \frac{4\alpha^3}{(2+\alpha)(2-1\alpha)^2}\left(\frac{P}{P°}\right)$. As $P° = 1$ bar, and since the total pressure is also 1 bar, all the pressures disappear: $K = \frac{4\alpha^3}{(2+\alpha)(2-2\alpha)^2}$. Since the reaction has gone to 0.6215% completion, then α = 0.006215, and you find $K = 1.2116 \times 10^{-7}$. Last is $\Delta_r G$, due to the relationship $\Delta G = \Delta_r G + RT\cdot\ln(K)$, we know that:

$\Delta G = -RT\cdot\ln(K) = -8.314\ \text{J/K/mol} \times 2000\ \text{K} \times \ln(1.2116\times10^{-1}) = 2.6482\times10^5\ \text{J} = 264.82\ \text{kJ}$. Note a neat little fact- this reaction represents dissociating two moles of gas-phase water from its elements. You may recall in an earlier example problem that $\Delta_r G(2000\ \text{K}) = +132.41\ \text{kJ}$ for the dissociation of one mole of gas phase water into hydrogen and oxygen. Thus, dissociating two moles would be: 2 × 132.41 kJ = 264.82 kJ, the same number!

$$\Delta_r G = \sum_{\text{products}} \upsilon_i \cdot \mu_i - \sum_{\text{reactants}} \upsilon_i \cdot \mu_i$$

$$= \left(\sum_{\text{products}} \upsilon_i \cdot \mathring{\mu}_i - \sum_{\text{reactants}} \upsilon_i \cdot \mathring{\mu}_i \right) + RT \cdot \ln \left[\frac{\prod_{\text{products}} \left(\frac{\chi_i \cdot P}{P^\circ} \right)^{\upsilon_i}}{\prod_{\text{reactants}} \left(\frac{\chi_i \cdot P}{P^\circ} \right)^{\upsilon_i}} \right]$$

The argument of the natural log has a name. Specifically, at the beginning of a reaction, it is called the reaction quotient and is symbolized using the letter "Q". If the ratio is determined at equilibrium, it is called the equilibrium constant and is called "K". Consequently, at equilibrium:

$$K = \exp\left(- {\left(\sum_{\text{products}} \upsilon_i \cdot \mu_i - \sum_{\text{reactants}} \upsilon_i \cdot \mu_i \right)} \Big/ {RT} \right) = \exp\left(- {\Delta_r G^\circ} / {RT} \right)$$

To summarize, chemical potentials determine when a reaction has reached equilibrium, which in turn allows us to calculate reaction yields. The chemical potential is dependent on the partial pressure of a gas, which is basically the same thing as its concentration. The chemical potential is larger when the concentration is high. The potentials of reactants and products are modulated throughout a reaction as a result. Two example problems are provided below, and due to the complexity of calculating reaction yields we will work two of the more difficult examples that you could possibly run into.

6.5.1 Temperature dependent equilibrium constants. As shown in the previous example, the equilibrium constant depends on the temperature because the Gibbs energy is temperature dependent. It turns out that we can quickly calculate the temperature dependence of the equilibrium constant via the Gibbs-Helmholtz equation; given that at equilibrium:

$$\Delta_r G^\circ = -RT \cdot \ln(K)$$

Here, you should know that if you use the standard state for this calculation, then T must be the standard state temperature 25 °C. We need to perform some mathematical manipulations as a result to see the real temperature dependence. First, we rearrange the above as: $\ln(K) = \frac{-\Delta_r G^\circ}{RT}$, the derivative of which is:

$$\frac{\partial \ln(K)}{\partial T} = \frac{1}{R} \frac{\partial \, {-\Delta_r G^\circ}/{T}}{\partial T} = \frac{\Delta_r H^\circ}{RT^2}$$

using the Gibbs-Helmholtz equation. Now we rearrange the partials $\partial \ln(K) = \frac{\Delta_r H^\circ}{RT^2} \partial T$ and integrate:

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

The result of which is:

$$\ln[K(T_2)] = \ln[K(T_1)] - \frac{\Delta_r H^\circ}{R}\left(\frac{T_1 - T_2}{T_2 \cdot T_1}\right)$$

where T_1 is 298.15 K if our equilibrium constant and reaction enthalpy are defined from standard state conditions which is most typical. Note that we did make a simplification, which is that we did not include any temperature dependence to the enthalpy. This isn't impossible but does make the final result overly complex so we will simply make this approximation here.

Conclusion. In this chapter we showed how the absolute value of energy of a real chemical substance is unfortunately unknowable, which forces us to examine all thermodynamic processes as occurring relative to a standard state. We can use these data to predict reaction yields with good accuracy, albeit in a decently complex series of calculations especially if we are not using standard state conditions. 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.

Problems: Numerical

1. In the case that heat capacity varies with temperature to a degree that you should not neglect it, you can use the formula $C_{V,m} = a + bT + \frac{c}{T^2}$. The constants for CO_2 are a=35.9 J/K/mol, b=2.51×10^{-3} J/K^2/mol, and c = -8.62×10^{5} J·K/mol. What is the change in entropy of CO_2 as 1.0 mole is heated from 25 °C to 100 °C at constant volume? Hint: Start with $\partial S = \partial q_{rev}/T$, and the answer is +6.49 J/K. **(7 pts)**

2. What is the change in enthalpy for the explosion of TNT ($C_7H_5N_3O_6(s)$) given that: $\Delta_f H_m^\circ$ ($C_7H_5N_3O_6(s)$) = -63.2 kJ/mol. Hint: the reaction is $2\ C_7H_5N_3O_6(s) \rightarrow 3\ N_2(g) + 5\ H_2O(g) + 7\ CO(g) + 7\ C(s)$ **(5 pts)**

3. a. Why is it that: $\Delta_f H_m^\circ - T \times S_m^\circ$ = -46.11 kJ/mol – 298.15 K × 192.45 J/K/mol = -103.5 kJ/mol for $NH_3(g)$, but the data table in the book has $\Delta_f G_m^\circ$ =-16.45 kJ/mol? hint, don't answer this question yet. do pt. b and c first

b. Can you calculate $\Delta_f S_m^\circ$ for forming ammonia from its elements?

c. Now, calculate: $\Delta_f H_m^\circ - T \times \Delta_f S_m^\circ$, where $\Delta_f S_m^\circ$ is the same as in b.

d. Given that you got $\Delta_f H_m^\circ - T \times \Delta_f S_m^\circ$ = -16.48 kJ/mol in pt. c, go back and answer question a. FYI: This isn't a question. **(9 pts)**

4. a. Why is it that $\Delta_f H_m^\circ - T \times S_m^\circ$ = -2222 kJ/mol – 298.15 K × 360.2 J/K/mol = -2329 kJ/mol for sucrose, but $\Delta_f G_m^\circ$ of the same is -1543 kJ/mol? hint, do pt. b first

b. Can you calculate $\Delta_f S_m^\circ$ for forming sucrose from its elements (i.e. sucrose – carbon, hydrogen, and oxygen)?

c. Now, calculate: $\Delta_f H_m^\circ - T \times \Delta_f S_m^\circ$, where $\Delta_f S_m^\circ$ is the same as in b.

d. Given that you got $\Delta_f H_m^\circ - T \times \Delta_f S_m^\circ$ = -1543 kJ/mol in pt. c, go back and answer question a.

FYI: This isn't a question. **(9 pts)**

5. a. Steam reforming is used to make hydrogen for the production of ammonium for fertilizer. Can you please calculate $\Delta_r S^\circ$ and $\Delta_r G^\circ$ at standard temperature and pressure for the following reaction: $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$ **(6 pts)**

b. Using the data above, can you calculate $\Delta_r H^\circ$ as well? **(3 pts)**

c. How does it compare to calculating $\Delta_r H^\circ$ from value in the textbook's table? **(3 pts)**

6. What is the change in Gibbs free energy of forming octane from carbon and hydrogen given: $\Delta_r G^\circ$ from the combustion of octane (-5641.4 kJ), $\Delta_f G_m^\circ$ of CO_2 (-394.36 kJ/mol), and $\Delta_f G_m^\circ$ of liquid water (-237.13 kJ/mol)? These are all standard state values: **(5 pts)**

$C_8H_{18}(g) + 25/2\ O_2(g) \rightarrow 8\ CO_2(g) + 9\ H_2O(l)$ $\Delta_r G^\circ$ = -5641.4 kJ
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta_f G_m^\circ$ = -394.36 kJ/mol
$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ $\Delta_f G_m^\circ$ = -237.13 kJ/mol

Hint: You will need to do a lot of rearranging…

7. Now let's do the same problem with $\Delta_r H^\circ$ and $\Delta_r S^\circ$ using the following information:

$C_8H_{18}(g) + 25/2O_2(g) \rightarrow 8CO_2(g) + 9H_2O\ (l)$ $\Delta_r S^\circ$= -1104.0 J/K $\Delta_r H^\circ$=-5970.6 kJ
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta_f S_m^\circ$= 2.862 J/K/mol $\Delta_f H_m^\circ$=-393.51 kJ/mol
$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$ $\Delta_f S_m^\circ$= -163.34J/K/mol $\Delta_f H_m^\circ$=-285.83 kJ/mol

Here, calculate $\Delta_f H_m^\circ$ and $\Delta_f S_m^\circ$ for the formation of octane, and show that your answer for $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \times \Delta_f S_m^\circ$ is the same (or very close to it) for question 6 above. Hint: what temperature due you use? **(10 pts)**

8. Kirchoff's Law in its most complex form is:

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

What I like about this is that it is basically equal to: $\Delta_r G(T_2) = \Delta_r H(T_2) - T_2 \times \Delta_r S(T_2)$

where the change in ΔH and ΔS with temperature are taken into account using the various formula with $\Delta_r C_P^\circ$. However- there is one small approximation (one itty-bitty fact is being ignored)- what is it? **(2 pts)**

9. We need to synthesize ammonia gas to make a huge refrigerator, so we hydrolyze urea: $(NH_2)_2CO_{(s)} + H_2O_{(l)} \rightarrow 2NH_{3(g)} + CO_{2(g)}$. Unfortunately, $\Delta_r G^\circ = +7.27$ kJ, and the reaction is not spontaneous. What would I get if I calculated $\Delta_r G$ at 50 °C? Hint: $\Delta_r H^\circ = 133.2$ kJ and $\Delta_r S^\circ = 424.53$ J/K according to the data tables. **(15 pts)**

10. There is an approximation to doing Kirchoff's Law calculations based on the Gibbs-Helmholtz relation: $\left.\frac{\partial \Delta G/_T}{\partial T}\right)_P = -\frac{\Delta H^\circ}{T^2}$. Moving the partials yields: $\partial\, {}^{\Delta G}/_T = -\frac{\Delta H^\circ}{T^2}\partial T$. Now can you please integrate the equation to determine approximately how to calculate ΔG at a different temperature other than 25 °C? **(5 pts)**

11. We need to synthesize ammonia gas to make a huge refrigerator, so we hydrolyze urea: $(NH_2)_2CO_{(s)} + H_2O_{(l)} \rightarrow 2NH_{3(g)} + CO_{2(g)}$. Unfortunately, $\Delta_r G^\circ = +7.27$ kJ, and the reaction is not spontaneous. What would I get if I calculated $\Delta_r G$ at 100 °C?

a. Use the "simplified" equation: $\frac{\Delta_r G(T_2)}{T_2} = \frac{\Delta_r G^\circ}{298.15\text{ K}} + \Delta_r H^\circ\left(\frac{1}{T_2} - \frac{1}{298.15\text{ K}}\right)$ **(5 pts)**

b. Now use the "harder", yet more accurate equation:

$\Delta_r G(T_2) = \Delta_r H^\circ + \Delta_r C_P^\circ \times (T_2 - 298.15K) - T_2 \times \left(\Delta_r S^\circ + \Delta_r C_P^\circ \times \ln\left(\frac{T_2}{298.15K}\right)\right)$ **(10 pts)**

Hint: $\Delta_r H^\circ$= 133.2 kJ and $\Delta_r S^\circ = 424.53$ J/K according to the data tables. Note that you need to determine one more thing from the data tables…

12. If we estimate $\Delta_r G$ at 50 °C for the hydrolysis of urea to form ammonia from the following:

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

where $\Delta_r G^\circ$= +7.27 kJ and $\Delta_r H^\circ = 133.2$ kJ how far off from the real answer of: $\Delta_r G = -3.92$ kJ are we? **(5 pts)**

13. I looked up that $\Delta_r G$ is -1.0 kJ/mol for the following reaction:

A(g) + B(g) ↔ C(g) + D(g)

How much has this reaction proceeded if you start with n moles of both reactants, assuming the pressure is 1 bar and let's say temperature is 25 °C? **(10 pts)**

Here is a hint: starting with the normal table:

	A	B	C	D
Amount at equilibrium	$n(1-\alpha)$	$n(1-\alpha)$	$n\alpha$	$n\alpha$
Mole fractions	$\frac{n(1-\alpha)}{2n}$	$\frac{n(1-\alpha)}{2n}$	$\frac{n\alpha}{2n}$	$\frac{n\alpha}{2n}$
Partial pressures	$\frac{(1-\alpha)}{2}P$	$\frac{(1-\alpha)}{2}P$	$\frac{\alpha}{2}P$	$\frac{\alpha}{2}P$

where α represents the extent of the reaction (this is what I am asking you to calculate). Note the total number of moles, regardless of the extent of the reaction, is 2n. Now at equilibrium:

K = $\prod_i \frac{P_i^{\upsilon_i}}{P^{\circ \upsilon_i}}$, where P_i is the partial pressure of species i. As usual, P° is just 1 bar. K is now: $\frac{\left(\frac{\alpha}{2} \cdot \frac{P}{P^\circ}\right)\left(\frac{\alpha}{2} \cdot \frac{P}{P^\circ}\right)}{\left(\frac{(1-\alpha)}{2} \cdot \frac{P}{P^\circ}\right)\left(\frac{(1-\alpha)}{2} \cdot \frac{P}{P^\circ}\right)}$.

Simplification gives: $\left(\frac{2}{(1-\alpha)} \cdot \frac{P^\circ}{P}\right)^2 \left(\frac{\alpha}{2} \cdot \frac{P}{P^\circ}\right)^2 = \frac{4\alpha^2}{4(1-\alpha)^2} = \frac{\alpha^2}{1-2\alpha+\alpha^2}$.

Now when you plug this into the expression for the Gibbs energy at equilibrium: $\ln\left(\frac{\alpha^2}{1-2\alpha+\alpha^2}\right) = \frac{-\Delta_r G^\circ}{RT}$, you can solve for α. Hint: if $A\alpha^2 + B\alpha + C = 0$, then the two possible values of α are: $\frac{-B+\sqrt{B^2-4AC}}{2A}$ or $\frac{-B-\sqrt{B^2-4AC}}{2A}$. One of them is correct, the other yields a nonsensical answer. Remember α ranges from 0 to 1.

14. One of the most widely produced chemicals in the world is ammonium to be used as fertilizer. It is synthesized by the Haber process (ΔG° = –32.9 kJ/mol):

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

How much does this reaction proceeded if you start with n moles of nitrogen and 3n moles of hydrogen? Also, let's assume that the reactor maintains a pressure of 1 bar like the reaction is in a balloon. Also let's say temperature is maintained at 25 °C. **(10 pts)**

Hint: starting with the normal table:

	N_2	H_2	NH_3
Amount at equilibrium	$n(1-\alpha)$	$3n(1-\alpha)$	$2n\alpha$
Mole fractions	$\frac{n(1-\alpha)}{4n-2n\alpha}$	$\frac{3n(1-\alpha)}{4n-2n\alpha}$	$\frac{2n\alpha}{4n-2n\alpha}$
Partial pressures	$\frac{(1-\alpha)}{4-2\alpha}P$	$\frac{3(1-\alpha)}{4-2\alpha}P$	$\frac{2\alpha}{4-2\alpha}P$

where α represents the extent of the reaction. K = $\prod_i \frac{P_i^{\upsilon_i}}{P^{\circ \upsilon_i}}$, where P_i is the partial pressure of species i. As usual, P° is just 1 bar. K is now: $\frac{\left(\frac{2\alpha}{4-2\alpha} \cdot \frac{P}{P^\circ}\right)^2}{\left(\frac{(1-\alpha)}{4-2\alpha} \cdot \frac{P}{P^\circ}\right)\left(\frac{3(1-\alpha)}{4-2\alpha} \cdot \frac{P}{P^\circ}\right)^3}$. Simplification gives:

$$\left(\frac{2\alpha}{4-2\alpha} \cdot \frac{P}{P^\circ}\right)^2 \left(\frac{4-2\alpha}{(1-\alpha)} \cdot \frac{P^\circ}{P}\right) \left(\frac{4-2\alpha}{3(1-\alpha)} \cdot \frac{P^\circ}{P}\right)^3 = \frac{16\alpha^2(2-\alpha)^2}{27(1-\alpha)^4} \cdot \frac{P^{\circ 2}}{P^2}.$$

Now since the pressure is maintained at 1 bar and the standard pressure is 1 bar, we can eliminate the pressure component on the right side and are thus left with:

$K = \frac{16\alpha^2(2-\alpha)^2}{27(1-\alpha)^4}$. Now when you plug this into the expression for the Gibbs energy at equilibrium: $\ln\left(\frac{16\alpha^2(2-\alpha)^2}{27(1-\alpha)^4}\right) = \frac{-\Delta_r G^\circ}{RT}$, you can solve for α given that ΔG° = –32.9 kJ/mol.

Hint-hint: Use the Wolfram equation solver web site: http://www.wolframalpha.com/

For example, to solve the following equation: $(1-1.497)\alpha^2 + 2 \cdot 1.497\alpha - 1.497 = 0$

Input this into the link above: (1-1.497)*x^2+2*1.497*x-1.497=0

There is a lot of things that are returned, but among them is:

Solutions:

$x = 0.550263$

$x = 5.47388$

There are two answers since this is a quadratic equation. Now do the same for:

$\ln\left(\frac{16\alpha^2(2-\alpha)^2}{27(1-\alpha)^4}\right) = \frac{-\Delta_r G°}{RT}$ to solve for α. You will also get two answers; make sure you pick the right one.

15. If the reactor in question 14 above didn't maintain a pressure of 1 bar, what would be your expression for $K = \frac{16\alpha^2(2-\alpha)^2}{27(1-\alpha)^4} \cdot \frac{P°^2}{P^2}$ and what would be the extent of the reaction (i.e. use the Wolfram web site to recalculate α)?

Hint: P° is 1 bar so it doesn't matter. The pressure P will drop from 1 bar to ½ bar since you go from 4 moles of gas to 2 moles. What function of α gives $P(\alpha) = 1$ if $\alpha=0$ and $P(\alpha)=0.5$ if $\alpha = 1$? **(10 pts)**

16. At 1 bar of pressure and 2000 K, water has dissociated by 0.6215% at equilibrium via:

$H_2O_{(g)} \leftrightarrow H_{2(g)} + ½O_{2(g)}$. What is K, $\Delta_r G$, $\Delta_r G°$? **(10 pts)**

17. a. If the equilibrium constant (K) for water dissociation: $H_2O_{(g)} \leftrightarrow H_{2(g)} + ½O_{2(g)}$ is 3.4808×10^{-4} at 2000 K, what is the equilibrium constant at room temperature? FYI: $\Delta_r H° = 241.82$ kJ/mol; let's assume that it is temperature-invariant. **(6 pts)**

b. What is the corresponding $\Delta_r G°$? **(4 pts)**

c. Why is there a slight difference in your answer in **b.** from $-\Delta_f G_m^{\circ}$= 228.572 kJ/mol, which is the accepted value (i.e. the number you find in thermo data tables)? **(2 pts)**

Problems: Theoretical or Explain in Words

1. When I look at a table of standard entropies, I see that cyclohexane $C_6H_{12(l)}$ has a S_m° = 204 J/K/mol while pentane $C_5H_{12(g)}$ has S_m° = 384 J/K/mol. This seems like nonsense, as cyclohexane has a higher heat capacity (157 J/K/mol) vs. pentane (120 J/K/mol), and entropy is roughly proportional to heat capacity (remember S is $\sim C_P\Delta T$). Tell me why does cyclohexane have much less entropy when it has a higher heat capacity? **(3 pts)**

2. Formic acid is found in the venom of poisonous animals, and formaldehyde is upregulated due to malnutrition. When I look at a table of standard entropies, I see that formic acid $CH_2O_{2(l)}$ has a S_m° = 129.0 J/K/mol while formaldehyde $CH_2O_{(g)}$ has S_m° = 218.8 J/K/mol. This seems like nonsense, as formic acid has a ***much higher*** heat capacity than formaldehyde (99 J/mol/K vs. 35.4 J/mol/k) it seems that formaldehyde should have more entropy (remember S is $\sim C_P\Delta T$). Is there a sensible reason why they are so different? **(3 pts)**

3. In question 5 of the numerical problems, you found that the change in the entropy of the reaction is ~215 J/K/mol. Why does this make sense? **(3 pts)**

4. Why does it make sense that heating up the reaction in questions 9 & 10 of the previous section causes ΔG to become negative? **(3 pts)**

5. In the text we showed that: $\partial U = -P\,\partial V + T\,\partial S + \frac{\partial U}{\partial n}\Big)_{V,S}\partial n$ and: $\partial H = V\,\partial P + T\,\partial S + \frac{\partial H}{\partial n}\Big)_{P,S}\partial n$ to show that: $\frac{\partial H}{\partial n}\Big)_{P,S} = \frac{\partial U}{\partial n}\Big)_{V,S}$. Can you now prove: $\frac{\partial A}{\partial n}\Big)_{V,T} = \frac{\partial U}{\partial n}\Big)_{V,S}$? Hint: start with $\partial A = \partial U - \partial(TS)$ **(7 pts)**

6. I was doing a thermo derivation once where I determined that:
$\int_{298.15K}^{T_2} \frac{-\Delta H°}{T^2} = \Delta H° \left[\frac{1}{T_2} - \frac{1}{298.15K}\right]$. I made an approximation; what is it? **(3 pts)**

7. In question 15 in the previous section, why did I find that the extent of the reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is α=0.968 if the pressure is maintained at 1 bar but drops slightly to α=0.956 if the pressure drops to 0.5 bar? **(5 pts)**

8. When you integrate the Gibbs-Helmholtz relation: $\frac{\partial\, {}^{\Delta G}/_{T}}{\partial T}\Big)_P = -\frac{\Delta H°}{T^2}$ without considering the temperature dependence to ΔH, you are doing the same thing as calculating ΔG at a new temperature T_2 via: $\Delta G(T_2) = \Delta H° - T_2 \times \Delta S°$. Now, this gets a lot harder- let's integrate the Gibbs-Helmholtz relation to find $\Delta G(T_2)$ where we do take into account the temperature dependence to ΔH via: $\Delta H(T) = \Delta H° + \Delta C_P^{\circ} \times (T - 298.15)$.

Also recall that $\int_{\Delta G°/T_1}^{\Delta G(T_2)/T_2} \partial\, {}^{\Delta G}/_{T} = \frac{G(T_2)}{T_2} - \frac{\Delta G°}{T_1}$, where $\frac{\Delta G°}{T_1} = \frac{\Delta G°}{298.15K} = \frac{\Delta H° - 298.15K \times \Delta S°}{298.15K}$. This should give you a very accurate formula for $\Delta G(T_2)$. **(15 pts)**

Chapter 7: Solutions and Colligative Properties

Thus far we have only been examining gas phase expansions and contractions as a piston does work, including gas phase chemical reactions. For many years physical chemists largely studied gas phase chemistry, but many important things happen in condensed phases (liquid and solid) such as the geological creation of oil from ancient carbon or the solid phase synthesis of DNA. How do we begin to analyze the thermodynamics of chemicals that are not in the gas phase? 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°), and you can simply look them up. You can also sit down and watch the cup of water, but probably there isn't much to analyze (and the teaspoon of salt is doing even less- don't waste your time!). It's all, rather… boring.

Now let's do something much more fun! Take the teaspoon of salt and add it to the water, and see what happens- will the salt dissolve? Will the water get warm or 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 together. As you can imagine, this could be extremely complicated. Initially the water molecules interacted with each other, and this is still true after mixing, but now the water also interacts with the salt that was mixed in.

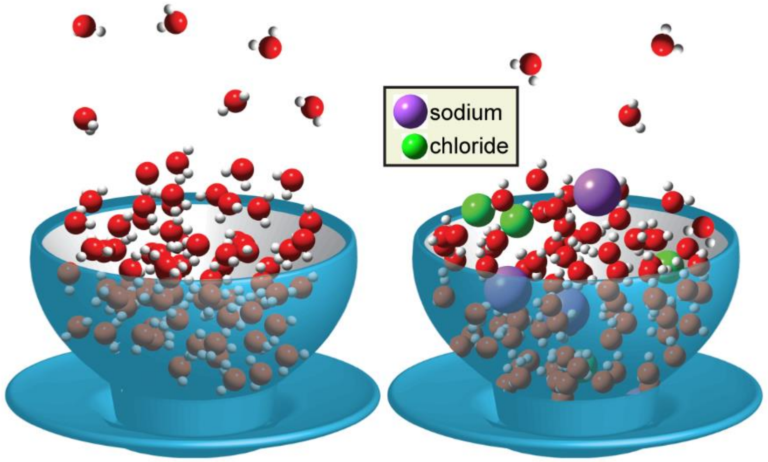


Figure 7.1. Vapors evlolve from the surface of water (left). Addition of NaCl can hinder water evaporation (right), by crowding the molecules or by forming a surface barrier.

Also the salt dissociates into ions (Na^+ and Cl^- for example); surely there are energetic and entropic consequences for that. 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 analyzing the liquid solution altogether.

Fortunately, there is a much easier way to study the thermodynamics of how things mix, which is to 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 potential which is the most important. Concerning the mixing of salt and water, we need to know how much the chemical potential of water drops due to the addition of salt. To do so we can simply measure the change of the chemical potential of the water vapor, which is in equilibrium with the liquid. Due to the equilibrium, the change in the vapor's chemical potential is exactly the same as that experienced by the liquid due to mixing. Walla! The very complex thermodynamics of the mixing in the liquid phase comes down to measuring the thermodynamic changes in the vapor (i.e. gas) state, which is what we have been doing exclusively thus far in this book.

How do we measure the chemical potential of a vapor? What do we expect about the vapor to change when its liquid component mixes with something else like salt or another liquid to form a solution? Using liquid water at room temperature and pressure as an example, we know that drawing a bath in a very dry room will result in evaporation. This continues until the partial water vapor pressure reaches 3,200 Pa (~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 which is how a system resists change. Thus, the partial pressure of water vapor will decrease. The change in partial pressure allows us to calculate $\Delta_{\text{mix}}\mu$ for the liquid.

Another way to view this is to question what happens if, in a very dry room, we add salt first to the bathtub and then add the water. Of course some of the water will vaporize, but to a smaller extent than expected without the salt. Here, we can think of the salt as forming a barrier at the surface of the liquid, which hinders water from vaporizing off as shown in Figure 7.1. 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 is ~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 since 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 more concerned with pressure rather than volume, we insert the perfect gas law to show:

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

where P_2 is the vapor pressure of the salted water and P_1 is from pure water. When we divide by n we can then calculate the change in chemical potential:

$$^{\Delta G}/_{n} = \Delta\mu = RT \cdot \ln\left(\frac{P_2}{P_1}\right)$$

Some notational changes are needed because we are discussing mixtures. Specifically, we will call $P_2 = P_i$, 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 P_1 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:

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

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 via 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 such as gin and juice (ethanol and water), and measure the changes in the individual substances' vapor pressures to determine ΔG_m, ΔH_m, and ΔS_m for mixing. However, the measurement of partial pressure of a vapor is rather complex even by today's standards. Perhaps there is a way to relate the partial pressure of the vapor to the concentration of the liquid

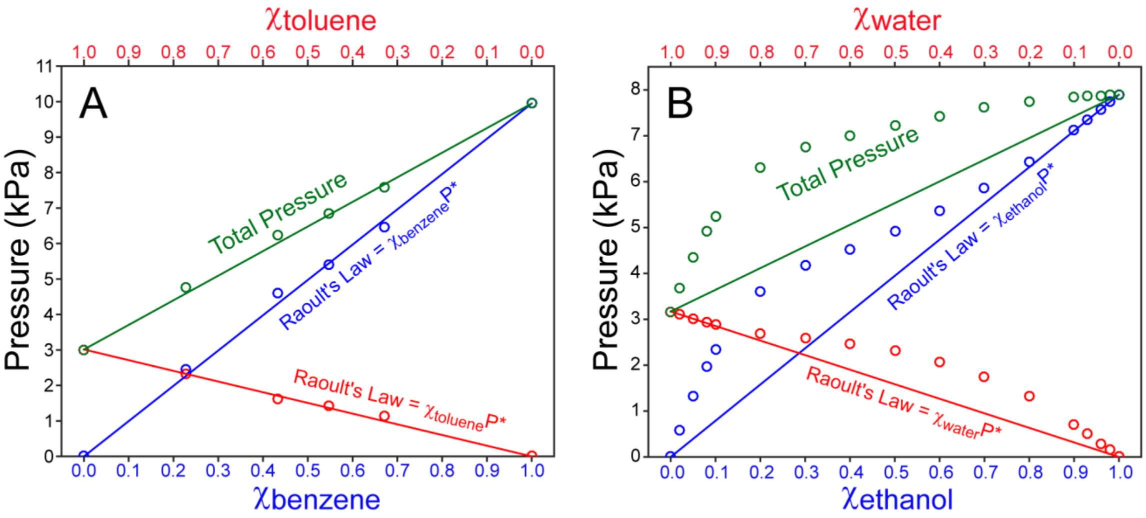


Figure 7.2. A. The partial pressures of benzene and toluene and **B.** water and ethanol in a liquid mixture. Data are circled, lines are from Raoult's Law.

in solution? For example, if we dilute water with an extremely large quantity of ethanol then the water partial pressure should drop to nothing, i.e. ~0 Pa. If we have pure water, then the partial pressure is 3,200 Pa. Thus, the partial pressure changes from 0 Pa → 3,200 Pa as χ_{H2O} increases from 0 → 1.

François-Marie Raoult, an electrochemist, discovered that many liquid mixtures have partial pressures that are a linear functions of the molar concentrations, especially if one component is very dilute. Mathematically this is expressed as $P_i = P_i^* \cdot \frac{n_i}{n_{total}} = P_i^* \cdot \chi_i$. This statement constitutes Raoult's Law, and note how it yields the pure partial pressure if the ith species is pure ($\chi_i = 1$), and 0 Pa if the ith species is infinitely diluted ($\chi_i = 0$). Shown in Figure 7.2 A is a graph of the partial pressures of benzene and toluene as a function of their mole fractions, including lines derived from $P_i = P_i^* \cdot \chi_i$. Clearly, Raoult's Law 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; this will be discussed further in later sections.

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. Before further discussion, several new thermodynamic "excess functions" must be defined for liquid mixtures. For example, the volume per mole of liquid "A" in its pure form is $V_{m,A}$. In other words, if we have a glass full of liquid "A" and add one more mole of "A" to it, then we expect the volume to increase by $V_{m,A}$. As a result, we can state that $V_{m,A} = \left.\frac{\partial V}{\partial n_A}\right)_{P,T}$.

You are actually quite familiar with this concept- for example, if you add a mole of water to water, the volume increases by ~18 mL as this is the volume of 18 grams of H_2O. However, if the glass is full of liquid "B", then we might measure a different volume increase after addition of a mole of "A" which is designated as $\bar{V}_A = \left.\frac{\partial V}{\partial n_A}\right)_{P,T,n_B \neq n_A}$, where the subscript "$n_B \neq n_A$" means that we are studying a solution that has more than one component. For example, adding 1 mole of water to a large quantity of ethanol results in an increase in volume of ~14 mL. If the partial molar volume of "A" changes in the presence of "B" (i.e. $\bar{V}_A \neq V_{m,A}$), as in the case of adding water to ethanol, then there will be a non-zero excess mixing volume ($\Delta_{mix}V$), which is defined as:

$$\Delta_{mix}V = n_A(\bar{V}_A - V_{m,A}) + n_B(\bar{V}_B - V_{m,B})$$

where the n_A and n_B quantities 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 $\Delta_{mix}V$, after all we can't make a solution just out of liquid "A"!

The excess volumes $\bar{V}_A$ and $\bar{V}_B$ are functions of the composition of the liquid as shown in Figure 7.3, which are the partial volumes of water and ethanol in solution. First, note that the volume per mole of pure water is 18.07 mL/mol. Thus, the partial molar volume of water, when added to more water, is:

$$\bar{V}_{H_2O} = V_{m,H_2O} = 18.07 \text{ mL/mol}$$

(red curve of Figure 7.3). Clearly the excess mixing volume $\Delta_{mix}V$ = 0 mL/mol when adding water to water. However, when a mole of water is added to a very large quantity of ethanol, then we find that $\bar{V}_{H_2O}$= 14.09 mL/mol. Thus, addition of 1 mole of water to a large quantity of ethanol increases the volume by 14.09 mL, leading to an excess mixing volume of:

$$\Delta_{mix}V = -3.98 \text{ mL}$$

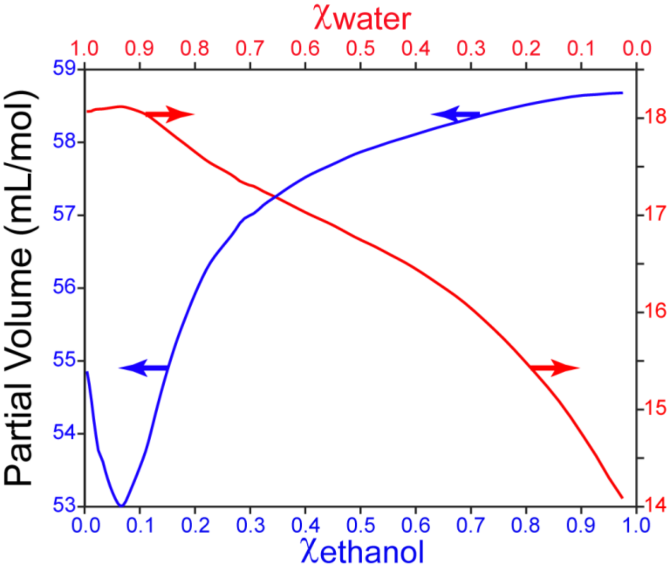


Figure 7.3. Partial volumes of an ethanol and water mixture. Note the separate y-axes.

Advanced Derivations: Gibbs-Duhem Equations

The partial volume data shown in Figure 7.3 appear as somewhat distorted mirror images of each other. This is the result of a Gibbs-Duhem equation. First, we take the formula for the change in the volume of a solution:

$$\partial \mathrm{V} = \frac{\partial \mathrm{V}}{\partial \mathrm{n_A}}\Bigg)_{\mathrm{P,T,n_B \neq n_A}} \partial \mathrm{n_A} + \frac{\partial \mathrm{V}}{\partial \mathrm{n_B}}\Bigg)_{\mathrm{P,T,n_A \neq n_B}} \partial \mathrm{n_B} =$$

$$\overline{\mathrm{V}}_\mathrm{A}\, \partial \mathrm{n_A} + \overline{\mathrm{V}}_\mathrm{B}\, \partial \mathrm{n_B}$$

Given that the partial quantities are extensive variables, we can integrate them all starting with a value of 0 as follows:

$$\int_0^{\mathrm{V}} \partial \mathrm{V} = \mathrm{V} = \int_0^{\mathrm{n_A}} \overline{\mathrm{V}}_\mathrm{A}\, \partial \mathrm{n_A} + \int_0^{\mathrm{n_B}} \overline{\mathrm{V}}_\mathrm{B}\, \partial \mathrm{n_B} = \overline{\mathrm{V}}_\mathrm{A} \mathrm{n_A} + \overline{\mathrm{V}}_\mathrm{B} \mathrm{n_B}$$

Here is an interesting trick- take the derivative of the above ($\mathrm{V} = \overline{\mathrm{V}}_\mathrm{A} \mathrm{n_A} + \overline{\mathrm{V}}_\mathrm{B} \mathrm{n_B}$) and don't forget the product rule:

$$\partial \mathrm{V} = \partial(\overline{\mathrm{V}}_\mathrm{A} \mathrm{n_A}) + \partial(\overline{\mathrm{V}}_\mathrm{A} \mathrm{n_A}) = \overline{\mathrm{V}}_\mathrm{A}\, \partial \mathrm{n_A} + \overline{\mathrm{V}}_\mathrm{B}\, \partial \mathrm{n_B} + \mathrm{n_A}\, \partial \overline{\mathrm{V}}_\mathrm{A} + \mathrm{n_B}\, \partial \overline{\mathrm{V}}_\mathrm{B}$$

Now we have a conundrum, which is how can it be simultaneously true that $\partial \mathrm{V} = \mathrm{V_A}\, \partial \mathrm{n_A} + \overline{\mathrm{V}}_\mathrm{B}\, \partial \mathrm{n_B}$ yet $\partial \mathrm{V} = \overline{\mathrm{V}}_\mathrm{A}\, \partial \mathrm{n_A} + \overline{\mathrm{V}}_\mathrm{B}\, \partial \mathrm{n_B} + \mathrm{n_A}\, \partial \overline{\mathrm{V}}_\mathrm{A} + \mathrm{n_B}\, \partial \overline{\mathrm{V}}_\mathrm{B}$? Its fairly easy, it must be true that $\mathrm{n_A}\, \partial \overline{\mathrm{V}}_\mathrm{A} + \mathrm{n_B}\, \partial \overline{\mathrm{V}}_\mathrm{B} = 0$. Consequently $\frac{\partial \overline{\mathrm{V}}_\mathrm{A}}{\partial \overline{\mathrm{V}}_\mathrm{B}} = -\frac{\mathrm{n_B}}{\mathrm{n_A}}$, and thus the partial volume of ethanol is the mirror image of the partial volume of water, weighted by the relative number of moles. This is exactly what is observed in Figure 7.3.

Likewise, the molar volume of pure ethanol is 58.7 mL/mol, but the partial molar volume decreases to $\overline{\mathrm{V}}_{\mathrm{EtOH}}$ = 54.9 mL/mol if adding ethanol to a large quantity water. In this situation $\Delta_{\mathrm{mix}}\mathrm{V} = -3.8$ mL. Figure 7.3 shows the partial molar volumes of ethanol and water as a function of solution composition, and it is no accident that the curves are nearly mirror images of each other. This is explained at the end of this chapter.

There are excess functions for all thermodynamic variables, which are listed below in a more generalized format:

$$\Delta_{\mathrm{mix}}\mathrm{U} = \sum_{\mathrm{i}=1}^{\alpha} \mathrm{n_i}\left(\overline{\mathrm{U}}_\mathrm{i} - \mathrm{U_{m,i}}\right)$$

$$\Delta_{\mathrm{mix}}\mathrm{H} = \Delta_{\mathrm{mix}}\mathrm{U} + \mathrm{P}\cdot\Delta_{\mathrm{mix}}\mathrm{V} = \sum_{\mathrm{i}=1}^{\alpha}\mathrm{n_i}\left(\overline{\mathrm{H}}_{\mathrm{i}} - \mathrm{H}_{\mathrm{m,i}}\right)$$

$$\Delta_{\mathrm{mix}}\mathrm{S} = \sum_{\mathrm{i}=1}^{\alpha}\mathrm{n_i}\left(\overline{\mathrm{S}}_{\mathrm{i}} - \mathrm{S}_{\mathrm{m,i}}\right)$$

$$\Delta_{\mathrm{mix}}\mathrm{G} = \Delta_{\mathrm{mix}}\mathrm{H} - \mathrm{T}\cdot\Delta_{\mathrm{mix}}\mathrm{S} = \sum_{\mathrm{i}=1}^{\alpha}\mathrm{n_i}\left(\overline{\mathrm{G}}_{\mathrm{i}} - \mathrm{G}_{\mathrm{m,i}}\right)$$

where we say that there are α number of components in the solution; generally we will use $\alpha = 2$ (for example, water and ethanol) for simplicity.

Now that excess functions are defined, we can examine what makes a solution as "ideal". Specifically, the components "A" and "B" of an ideal solution obey Raoult's Law, and have the following properties:

- The partial volumes of the components in solution are identical to their pure partial volumes.
- 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 if 12 oz. of "A" is mixed with 12 oz. of "B", then the result is a 24 oz. solution. Thus, $\Delta_{\mathrm{mix}}\mathrm{V} = 0\ \mathrm{m}^3$. The consequences of the second property is that the internal energy of molecule "A", when in it's pure form, is the same as when mixed with molecule "B". This means that $\Delta_{\mathrm{mix}}\mathrm{U} = 0\ \mathrm{J}$. Combining these properties allows us to determine the enthalpy of mixing: $\Delta_{\mathrm{mix}}\mathrm{H} = \Delta_{\mathrm{mix}}\mathrm{U} + \Delta_{\mathrm{mix}}(\mathrm{PV}) = \Delta_{\mathrm{mix}}\mathrm{U} + \mathrm{P}\cdot\Delta_{\mathrm{mix}}\mathrm{V}$ since we assume constant temperature and a constant external pressure of 1 bar. As ideal solutions have $\Delta_{\mathrm{mix}}\mathrm{U} = 0\ \mathrm{J}$ and $\Delta_{\mathrm{mix}}\mathrm{V} = 0\ \mathrm{m}^3$, it is true that ideal solutions have an excess mixing enthalpy of $\Delta_{\mathrm{mix}}\mathrm{H} = 0\ \mathrm{J}$. Thus, ideal solutions neither warm nor cool when "A" and "B" are mixed.

A great example of an ideal solution is the mixing of toluene and benzene, the data from which are shown in Figure 7.2 A. Our chemical intuition tells us that benzene and toluene likely interact both with each other and among themselves via pi-pi interactions, and the molecules have roughly the same volume. Hence, they form an ideal solution. It is clear from Figure 7.2 B that the data for both water and ethanol do not follow Raoult's Law. Consequently, water + ethanol do not form an ideal solution, and this is likely due to the disruption of water's hydrogen bonding by ethanol. Mixing water with ethanol results in a warm solution, which is not ideal.

Before we analyze the water + ethanol system further, let's take one last look at why ideal solutions mix, which must mean that $\Delta_{\text{mix}}G$ is negative. Since:

$$\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T \cdot \Delta_{\text{mix}}S$$

and $\Delta_{\text{mix}}H$ = 0 J, then it must be true that entropy is entirely responsible for ideal solution mixing, i.e. $\Delta_{\text{mix}}G = -T \cdot \Delta_{\text{mix}}S$. Clearly $\Delta_{\text{mix}}S$ is always positive, giving a negative $\Delta_{\text{mix}}G$. In fact, in sec. 7.1 we determined that the Gibb's energy change for component "A" in a mixture as: $\Delta G_A = n_A RT \cdot \ln\left(\frac{P_2}{P_1}\right)$; given that the initial pressure is the pure partial pressure ($P_1 = P_A^*$) and the final pressure is the partial pressure in the mixed state ($P_2 = P_A$), we are left with:$\Delta G_A = n_A RT \cdot \ln\left(\frac{P_A}{P_A^*}\right)$. If we insert Raoult's Law: $P_A = P_A^* \cdot \chi_A$, the change in Gibb's energy becomes:

$$\Delta G_A = n_A RT \cdot \ln\left(\frac{P_A^* \cdot \chi_A}{P_A^*}\right) = n_A RT \cdot \ln(\chi_A)$$

Now since there must be at least two species to form a mixture, we must add to this the change in chemical potential of species "B" to calculate the total change. First we write the expression for the change in Gibbs energy:

$$\Delta_{\text{mix}}G = \Delta G_A + \Delta G_A = n_A RT \cdot \ln(\chi_A) + n_B RT \cdot \ln(\chi_B)$$

Next, we divide the change in Gibbs energy by total number of moles to get the per molar value, which is equal to the change in chemical potential:

$$\frac{\Delta_{\text{mix}}G}{n} = \Delta_{\text{mix}}\mu = \Delta\mu_A + \Delta\mu_B = \frac{n_A}{n} RT \cdot \ln(\chi_A) + \frac{n_B}{n} RT \cdot \ln(\chi_B) =$$
$$RT \cdot \left(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)\right)$$

where the total number of moles is $n = n_A + n_B$.

Given the $\Delta_{\text{mix}}G_m = -T \cdot \Delta_{\text{mix}}S_m$ relation derived above, we can see that:

$$\Delta_{\text{mix}}S_m = -R \cdot \left(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)\right)$$

which is always a positive quantity, and reveals that ideal solutions always mix and that this is 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:

$$\Delta_{\text{mix}}S = -nR \cdot \left(\chi_A \ln(\chi_A) + \chi_B \ln(\chi_B)\right)$$

7.4 Henry's Law, Activity, and Ideal-Dilute Solutions. What we have learned from the discussion that the mixing of ideal solutions is an entropically driven process. However, as we see in Figure 7.2 B, not all liquid mixtures are ideal. In fact, many liquids don't mix at all!

What are the sources of non-ideality, and just how "bad" are the ideal approximations as expressed by Raoult's Law? To examine further, we will now study how to incorporate non-ideality into mixing solutions, beginning with Henry's Law.

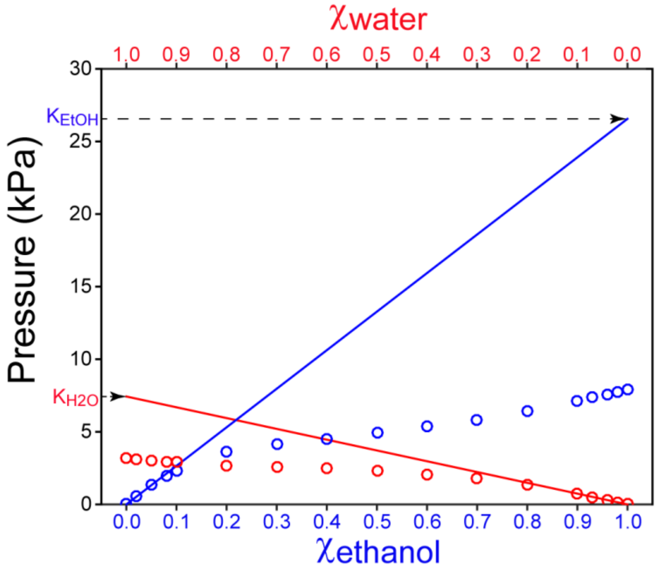


Figure 7.4. Linear fits to the partial pressures at low concentrations reveal the Henry's Law constants for water and ethanol.

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. The Henry's Law relationship can be used to determine the partial pressure of a vapor from the solute of a solution, where we define a solute as a highly diluted component of a liquid mixture. Mathematically Henry's Law is:

$$P_i = K \cdot \chi_i$$

where K is the Henry's Law constant of substance "i". The graph shown in Figure 7.4 reveals more clearly how this works, as it can be seen that the role of the Henry's Law constant is to act 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 liquid in solution. Since a solvent will generally follow Raoult's Law and the solute Henry's, we refer to such liquid mixtures as ideal-dilute solutions.

While Henry's Law doesn't provide significant insight into the thermodynamics of mixing, it does have great importance to 19th century bridge builders. At the turn of the last century many engineers had to work under high pressure environments (a diving bell- just google it) to build the foundations of bridges under the rivers that they spanned. If the workers were removed from the diving bell too quickly, they died from nitrogen gas release from their blood due to the fact that Henry's Law predicts that gas concentration (χ_i) in a liquid is proportional to the exterior pressure (P_i). Henry's Law is generally expressed in units of $mol \cdot L^{-1} atm^{-1}$, which yields the number of moles of dissolved gas when multiplied by the exterior pressure and solution's volume. Understanding the implications of Henry's Law in this regard is best developed by working a few problems found at the end of this chapter.

7.4.1 Activity. We There is an ultimate "fix" to the imperfections of Raoult's Law, which is to express the ratio of the measured partial pressure to the pure partial pressure $\left(\frac{P_i}{P_i^*}\right)$ in the expression of a solution's component's chemical potential: $\mu^* + \mathrm{RT} \cdot \ln\left(\frac{\mathrm{P_i}}{\mathrm{P_i^*}}\right)$ as:

$$\mu = \mu^* + \mathrm{RT} \cdot \ln(\mathrm{a_i})$$

where "$\mathrm{a_i}$" is the activity of component "i". To preserve a relationship to the mole fraction of the component in the liquid mixture, activity is often expressed as $a_i = \gamma_i \chi_i$ where γ_i is a correction factor such that $\frac{\mathrm{P_i}}{\mathrm{P_i^*}} = \gamma_i \chi_i$. As a result, the mixing excess Gibbs energy for a binary mixture of "A" and "B" is:

$$\Delta_{\mathrm{mix}}\mathrm{G} = \mathrm{nRT} \cdot \left(\chi_\mathrm{A} \cdot \ln(\gamma_\mathrm{A} \cdot \chi_\mathrm{A}) + \chi_\mathrm{B} \cdot \ln(\gamma_\mathrm{B} \cdot \chi_\mathrm{B})\right)$$

$$\Delta_{\mathrm{mix}}\mathrm{G} = \mathrm{nRT} \cdot \left(\chi_\mathrm{A} \cdot \ln(\gamma_\mathrm{A}) + \chi_\mathrm{B} \cdot \ln(\gamma_\mathrm{B}) + \chi_\mathrm{A} \cdot \ln(\chi_\mathrm{A}) + \chi_\mathrm{B} \cdot \ln(\chi_\mathrm{B})\right)$$

Calculating activities requires measuring all the partial pressures of the components of a solution, which is what we were trying to avoid using Raoult's Law. However, the fact that Raoult's Law doesn't work very well requires this approach.

7.4.1.1 Excess Enthalpy and Activity. Activity can be used to understand the origins of non-ideality of a solution. Since an ideal solution has $\Delta_{\mathrm{mix}}\mathrm{H} = 0\ \mathrm{J}$, a non-ideal solution must have a non-zero $\Delta_{\mathrm{mix}}\mathrm{H}$. In other words, when mixing two components of a non-ideal solution the mixture becomes warm or cold. As a result, we can create a phenomenological model for a non-zero $\Delta_{\mathrm{mix}}\mathrm{H}$, 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. Combining these effects leads to a model of $\Delta_{\mathrm{mix}}\mathrm{H} = \mathrm{nRT} \cdot \chi_\mathrm{A}\chi_\mathrm{B}$. However, we must allow both the sign and magnitude of the excess enthalpy to change. As a result, we will multiply this phenomenological relationship by "β", a fix-it factor, to yield:

$$\Delta_{\mathrm{mix}}\mathrm{H} = \beta \cdot \mathrm{nRT} \cdot \chi_\mathrm{A}\chi_\mathrm{B}$$

For an ideal solution $\Delta_{\mathrm{mix}}\mathrm{G} = \Delta_{\mathrm{mix}}\mathrm{H} - \mathrm{T} \cdot \Delta_{\mathrm{mix}}\mathrm{S} = -\mathrm{T} \cdot \Delta_{\mathrm{mix}}\mathrm{S}$ since $\Delta_{\mathrm{mix}}\mathrm{H} = 0\ \mathrm{J}$. If however we insert our phenomenological $\Delta_{\mathrm{mix}}\mathrm{H}$ into the same expression we find that:

$$\Delta_{\text{mix}}G = \beta \cdot nRT \cdot \chi_A\chi_B + nRT \cdot \left(\chi_A\ln(\chi_A) + \chi_B\ln(\chi_B)\right)$$

Now we do some factoring and multiply the last term by 1 = $(\chi_A + \chi_B)$:

$$\Delta_{\text{mix}}G = nRT \cdot \left(\beta \cdot \chi_A\chi_B(\chi_A + \chi_B) + \chi_A\ln(\chi_A) + \chi_B\ln(\chi_B)\right)$$

$$\Delta_{\text{mix}}G = nRT \cdot \left(\chi_A \cdot \beta \cdot \chi_B^2 + \chi_B \cdot \beta \cdot \chi_A^2 + \chi_A\ln(\chi_A) + \chi_B\ln(\chi_B)\right)$$

When compared to our previous relationship for $\Delta_{\text{mix}}G$ based on activity we see that:

$$\Delta_{\text{mix}}G = nRT\cdot (\chi_A \cdot \beta \cdot \chi_B^2 + \chi_B \cdot \beta \cdot \chi_A^2 + \chi_A \cdot \ln(\chi_A) + \chi_B \cdot \ln(\chi_B))$$

$$\Delta_{\text{mix}}G = nRT\cdot (\chi_A \cdot \ln(\gamma_A) + \chi_B \cdot \ln(\gamma_B) + \chi_A \cdot \ln(\chi_A) + \chi_B \cdot \ln(\chi_B))$$

it becomes clear 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, which is $P_A = K \cdot \chi_A$. If we take Henry's Law and divide by P_A^* we see that the ratio $\frac{P_A}{P_A^*} = K\frac{\chi_A}{P_A^*}$ for solute species "A" can be related to its activity $\frac{P_A}{P_A^*} = a_A = \gamma_A \cdot \chi_A = e^{\beta\chi_B^2} \cdot \chi_A$. Consequently, $K\frac{\chi_A}{P_A^*} = e^{\beta\chi_B^2} \cdot \chi_A$ 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:

$$K = P_A^* \cdot e^{\beta}$$

Thus, a non-zero excess enthalpy results in a modulation of the 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, but there is no good way to simply 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. In either case, the error results from the approximation that solutions are ideal as revealed by our model for the excess enthalpy generated by mixing two non-ideal liquids.

7.5 Colligative Properties. The 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.

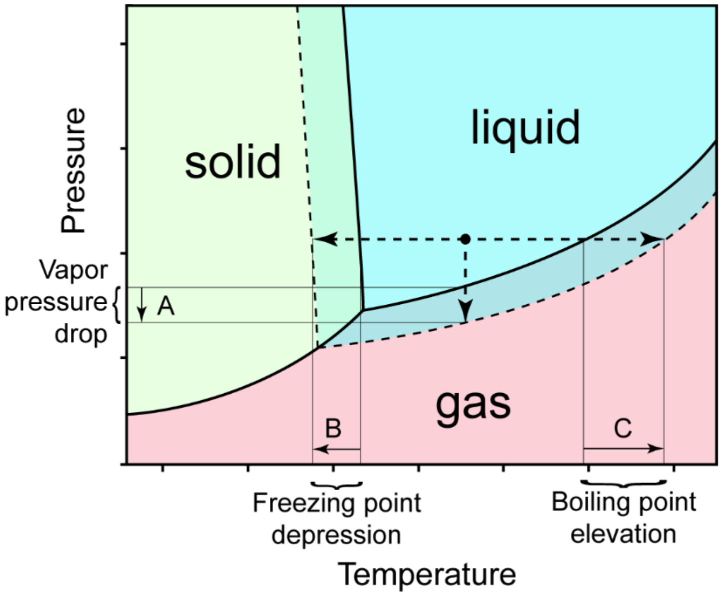


Figure 7.5. A phase diagram can be shifted to lower pressure and temperature to demonstrate the effects of solvent dilution (A) vapor pressure and (B) freezing depression, (C) boiling point elevation.

Now we will try to use our knowledge of the thermodynamics of mixtures to quantitatively predict these behaviors. For the most part, the accuracy of these relationships is modest, but they reveal what properties cause 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 properties of a liquid can be understood by measuring the changes in Gibbs Energy per mole (i.e. the chemical potential) of the vapor in equilibrium with the liquid. In fact, we have already shown how Raoult's Law predicts the lowering of a solvent's vapor pressure by addition of a solute:

$$\mathrm{P} = \mathrm{P}^* \cdot \chi_{\mathrm{liq}} = \mathrm{P}^* \cdot (1 - \chi_{\mathrm{salt}})$$

where χ_{liq} is the mole fraction of liquid water and χ_{salt} is the same 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}.

7.5.1.1 Melting Point Depression. Concerning the lowering of melting point of a solution, we begin by stipulating that liquid and solid phases co-existing in equilibrium must have the same chemical potential:

$$\mu^{\circ}_{\mathrm{solid}} = \mu^{\circ}_{\mathrm{liq}}$$

From here on we will use an example of adding salt to an equilibrium solution of water with ice. First, the chemical potential of liquid water is lowered by the addition of a salt as stipulated by Raoult's Law. Next, the system adjusts to maintain equilibrium, which mathematically means:

$$\mu^{\circ}_{\mathrm{solid}} = \mu^{\circ}_{\mathrm{liq}} + \mathrm{RT} \cdot \ln(\chi_{\mathrm{liq}})$$

What is interesting is that we assume that the salt in the water doesn't affect the solid's chemical potential, which makes sense if the ions do not permeate into the ice.

Recall that the Gibb's energy of formation per mole at the standard state is the chemical potential: $\Delta_{\mathrm{f}}\mathrm{G}^{\circ}_{\mathrm{m}} = \mu^{\circ}$, and some simple manipulation yields:

$$\mu^{\circ}_{\mathrm{solid}} - \mu^{\circ}_{\mathrm{liq}} = -\Delta_{\mathrm{fus}}\mathrm{G}^{\circ}_{\mathrm{m}} = \mathrm{RT} \cdot \ln(\chi_{\mathrm{liq}})$$

where $\Delta_{\mathrm{fus}}\mathrm{G}^{\circ}_{\mathrm{m}} = \Delta_{\mathrm{f}}\mathrm{G}^{\circ}_{\mathrm{solid,m}} - \Delta_{\mathrm{f}}\mathrm{G}^{\circ}_{\mathrm{liq,m}}$ is the change in Gibbs energy per mole for fusion (note that fusion is the correct IUPAC word for melting). The above relationship can be simplified as:

$$\frac{-\Delta_{\mathrm{fus}}\mathrm{G}^{\circ}_{\mathrm{m}}}{\mathrm{RT}} = \ln(\chi_{\mathrm{liq}})$$

The equation above uses the standard state fusion Gibbs energy per mole, which is tabulated in thermodynamic data tables at P = 1 bar and T = 25 °C. However, ice and salty water are not at equilibrium at T = 25 °C! To demonstrate, if we input the thermochemical data for water and ice at the standard state ($\Delta_{\mathrm{fus}}\mathrm{G}^{\circ}_{\mathrm{m}}$ = +0.59 kJ/mol, T = 25 ºC), we find that the liquid mole fraction is $\chi_{\mathrm{liq}} = 1.27$. This is impossible because mole fractions can only vary between 0 → 1! Thus, we must use the $\Delta_{\mathrm{fus}}\mathrm{G}_{\mathrm{m}}$ that is correct for $\mathrm{T}_{\mathrm{fus}}$, the melting temperature. This is expressed as:

$$\frac{-\Delta_{\mathrm{fus}}\mathrm{G}_{\mathrm{m}}}{\mathrm{RT}_{\mathrm{fus}}} = \ln(\chi_{\mathrm{liq}})$$

Now the equation works just fine. To demonstrate, pure H_2O water and ice are in equilibrium at 1 bar pressure and 0 °C, which means that their chemical potentials are equal:

$$\mu_{\mathrm{solid}} - \mu_{\mathrm{liquid}} = \Delta_{\mathrm{f}}\mathrm{G}_{\mathrm{solid,m}} - \Delta_{\mathrm{f}}\mathrm{G}_{\mathrm{liq,m}} = \Delta_{\mathrm{fus}}\mathrm{G}_{\mathrm{m}} = 0\ \mathrm{J/mol}$$

As a result:

$$\frac{-\Delta_{\mathrm{fus}}\mathrm{G}_{\mathrm{m}}}{\mathrm{RT}_{\mathrm{fus}}} = 0 = \ln(\chi_{\mathrm{liq}})$$

This is only true if $\chi_{\text{liq}} = 1$, meaning that the liquid is perfectly pure! Of course it is, since only pure water and ice are at equilibrium at 0 °C! If you are confused by the fact that the mole fraction of the liquid is $\chi_{\text{liq}} = 1$ 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. 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.

As a mathematical description of the above involves changes in mole fractions, chemical potentials and temperature, we must use the calculus of derivatives to derive a proper relationship. But what relationship are we looking for? We know that adding salt, which lowers the mole fraction of water (χ_{liq}), changes the boiling temperature T_{fus}. Consequently, let's work on $\frac{\partial \text{T}_{\text{fus}}}{\partial \chi_{\text{liq}}}$. However, it turns out that it is much easier solve the inverse relationship $\frac{\partial \chi_{\text{liq}}}{\partial \text{T}_{\text{fus}}}$. To calculate this derivative we can use the fact that $\ln(\chi_{\text{liq}}) = \frac{\Delta_{\text{fus}}\text{G}_{\text{m}}}{\text{RT}_{\text{fus}}}$, which means that we are going to solve: $\frac{\partial \ln(\chi_{\text{liq}})}{\partial \text{T}_{\text{fus}}}$ rather than: $\frac{\partial \chi_{\text{liq}}}{\partial \text{T}_{\text{fus}}}$ because these derivative will basically behave the same and it is easy to solve $\frac{\partial \ln(\chi_{\text{liq}})}{\partial \text{T}_{\text{fus}}}$ via the Gibbs-Helmholtz equations:

$$\frac{\partial \ln(\chi_{\text{liq}})}{\partial \text{T}_{\text{fus}}} = \frac{\partial}{\partial \text{T}_{\text{fus}}}\left(\frac{-\Delta_{\text{fus}}\text{G}_{\text{m}}}{\text{RT}_{\text{fus}}}\right) = \frac{1}{\text{R}}\frac{\partial\left({}^{-\Delta_{\text{fus}}\text{G}_{\text{m}}}/_{\text{T}_{\text{fus}}}\right)}{\partial \text{T}_{\text{fus}}} = \frac{\Delta_{\text{fus}}\text{H}_{\text{m}}}{\text{RT}_{\text{fus}}^2}$$

Now 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 $\frac{\partial \ln(\chi_{\text{liq}})}{\partial \text{T}_{\text{fus}}}$ as so:

$$\partial \ln(\chi_{\text{liq}}) = \frac{\Delta_{\text{fus}}\text{H}_{\text{m}}}{\text{RT}_{\text{fus}}^2}\partial \text{T}_{\text{fus}}$$

The limits of integration allow us to specify an initial temperature and salt concentration, which we will use $\ln(\chi_{\text{liq}}) = 0$ for the initial mole fraction (because $\chi_{\text{liq}} = 1$ for pure liquids) and $\text{T}_{\text{fus}} = 273.15$ K for the initial temperature (because the melting temperature of pure water is 0

°C). The upper limits of integration are the natural log of the final molar concentration $\ln\left(\chi'_{\mathrm{liq}}\right)$ and the corresponding new melting temperature T'_{fus}. Starting with the left side:

$$\int_{0}^{\ln\left(\chi'_{\mathrm{liq}}\right)} \partial \ln\left(\chi_{\mathrm{liq}}\right) = \ln\left(\chi'_{\mathrm{liq}}\right)$$

We can simplify this result as: $\ln\left(\chi'_{\mathrm{liq}}\right) = \ln(1-\chi_{\mathrm{salt}}) \approx -\chi_{\mathrm{salt}}$.

And now we integrate the right side:

$$\int_{T_{\mathrm{fus}}}^{T'_{\mathrm{fus}}} \frac{\Delta_{\mathrm{fus}}H_m}{RT_{\mathrm{fus}}^2}\partial T_{\mathrm{fus}} = \frac{-\Delta_{\mathrm{fus}}H_m}{RT_{\mathrm{fus}}}\Bigg]_{T_{\mathrm{fus}}}^{T'_{\mathrm{fus}}} = \frac{-\Delta_{\mathrm{fus}}H_m}{R}\left(\frac{1}{T'_{\mathrm{fus}}} - \frac{1}{T_{\mathrm{fus}}}\right) = \frac{-\Delta_{\mathrm{fus}}H_m}{R}\left(\frac{T_{\mathrm{fus}} - T'_{\mathrm{fus}}}{T'_{\mathrm{fus}}T_{\mathrm{fus}}}\right)$$

$$= \frac{-\Delta_{\mathrm{fus}}H_m}{R}\left(\frac{\Delta T}{T'_{\mathrm{fus}}T_{\mathrm{fus}}}\right)$$

where $T_{\mathrm{fus}} - T'_{\mathrm{fus}} = \Delta T$. We can make a few simplifications; given the fact that the new melting temperature T'_{fus} is only slightly less that T_{fus}, then: $T'_{\mathrm{fus}}T_{\mathrm{fus}} \approx T_{\mathrm{fus}}^2$. This results in: $\frac{-\Delta_{\mathrm{fus}}H_m}{R}\left(\frac{\Delta T}{T_{\mathrm{fus}}^2}\right) = -\chi_{\mathrm{salt}}$ which rearranges and simplifies to:

$$\Delta T = \frac{R \cdot T_{\mathrm{fus}}^2 \cdot \chi_{\mathrm{salt}}}{\Delta_{\mathrm{fus}}H_m}$$

As you work some practice problems using this formula, you will find that it is decently accurate but not perfect. This clearly has to do with the approximations made in the derivation, especially as we did not account for the temperature dependence of $\Delta_{\mathrm{fus}}H_m$ when analyzing the $\int_{T_{\mathrm{fus}}}^{T'_{\mathrm{fus}}} \frac{\Delta_{\mathrm{fus}}H_m}{RT_{\mathrm{fus}}^2}\partial T_{\mathrm{fus}}$ 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 $CaCl_2$; 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:

$$\Delta T = \frac{RT_{\mathrm{vap}}^2 \cdot \chi_{\mathrm{salt}}}{\Delta_{\mathrm{vap}}H_m}$$

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.

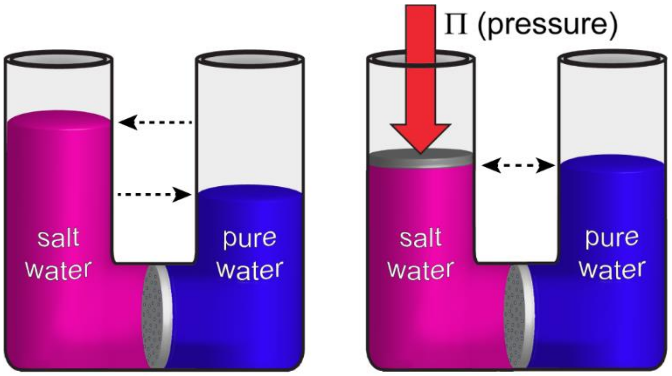


Figure 7.6. Salty and pure water connected by a semi-permeable membrane results in osmosis that displaces the liquid levels (left), the pressure from which can be measured by applying Π pressure (right).

Osmotic pressure is applicable to cells, which experience a higher internal pressure due to the fact that the 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 solution (left) is vertically displaced in a column by pressure. The "push" experienced by the left side is generated by osmosis from the pure water on the right side of a semi-permeable membrane such as a 2-dimensional phospholipid bilayer (these compose the surfaces of cells). There are two simple explanations for this observation. One is that the pure water on the right side is attempting to dilute the salty water via a Le Chatelier-type process, i.e. action to resist change. A more 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. The applied pressure necessary to even out the liquid column levels is the osmotic pressure (Π).

At equilibrium, the chemical potentials of the solution (assuming it's salt water) and pure water must be equal. However, there is a problem with the application of Raoult's Law. Accordingly, the chemical potential of the salt water solution: $\mu^* + RT \cdot \ln(\chi)$ is supposed to be equal to the chemical potential of pure water μ^* as:

$$\mu^* + RT \cdot \ln(\chi_{liq}) = \mu^*$$

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 Gibbs energy, which in fact comes from osmotic pressure. Recall that Gibbs energy per mol, which is the chemical potential, changes as:

$$\partial\mu = \partial G_m = -S_m\,\partial T + V_m\,\partial P$$

At a 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 as:

$$\mu^* + RT \cdot \ln(\chi_{liq}) + \Pi\frac{V}{n_{water}} = \mu^*$$

Some algebraic simplification yields:

$$\Pi\frac{V}{n_{water}} = -RT \cdot \ln(\chi_{liq})$$

As χ_{liq} is the mole fraction of the water solvent, then $\chi_{liq} = 1 - \chi_{salt}$ to which we can apply the approximation: $\ln(\chi_{liq}) = \ln(1 - \chi_{salt}) \approx -\chi_{salt}$. Inserting this into the relationship above:

$$\Pi V = n_{water}RT \cdot \chi_{salt}$$

Now we make one last approximation, which is that $\chi_{salt} = \frac{n_{salt}}{n_{water}+n_{salt}} \approx \frac{n_{salt}}{n_{water}}$ which is reasonable so long as $n_{salt} \ll n_{water}$. Next, we insert this into the expression for osmotic pressure:

$$\Pi V = n_{water}RT \cdot \chi_{salt} = n_{water}RT \cdot \frac{n_{salt}}{n_{water}} = n_{salt}RT$$

Finally, we have a fairly familiar-looking relationship:

$$\Pi V = n_{salt}RT$$

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, mostly liquids. Which is to say that we still apply the gas phase equations from earlier chapters, using chemical potential as a conduit to the thermodynamics of the condensed phase. In reality, we believe that the equations and concepts introduced here are fully correct, and that the activity of a solute conforms to the expected results. As a result, we would use the equations we developed here to define the activity, rather than use the activity to calculate the other thermodynamic variables. Regardless, this approach is justified by our demonstration of colligative properties for which we obtain reasonable predications consistent with measurements.

Problems: Numerical

1. Let's say that 1000 L of gasoline has spilled into the street (MW=117 g/mol, density=0.7 g/mL which is true for octane). What happens is firefighters add a lot of a material that dissolves into it that reduces the vapor pressure (liquid octane doesn't burn, only the vapors) which makes the spill a lot safer. In this case, the firefighters put 500 kg of a material into the gasoline and reduced its vapor pressure from the pure partial pressure of 10.0 kPa down to 8.0 kPa, which isn't high enough to burn. What is the molecular weight of the material that was added? (hint: use Raoult's Law, which relates changes in pressure to the mol fractions.) **(5 pts)**

2. Fizzle. **a.** Test your intuition- is the Henry's Law coefficient for a gas dissolved in water temperature dependent? **(1 pt)**

b. Let's say that the Henry's Law constant for CO_2 is 3×10^3 kPa · kg(H_2O) / mol(CO_2) at room temperature. Now if you open a bottle of Coke (12 oz), the pressure in the head space is 276 kPa. What is the volume of gas in mL that comes out once you open the bottle at 1 atm of pressure? Hint: 1 oz. is 30 cm^3. Just use the perfect gas law this time. **(5 pts)**

3. a. Let's say that the Henry's Law constant for N_2 is 1.56×10^5 kPa · kg(H_2O) / mol(N_2). How much N_2 is in a 40 kg diver's blood (a person is ~60%) at 100 m depth (which means that the diver is under 10.0 atms of pressure). Please answer in moles of gas. **(3 pts)**

b. Now the diver rapidly resurfaces to 1 atm of pressure; how much N_2 will come out of the diver's blood in Liters using the perfect gas law? **(3 pts)**

Hint: the reason you're calculating 3.82 L and not 3.43 L is that you forgot that some gas will be retained in the blood at 1 atm pressure.

c. Can you also show that the perfect gas law volume is basically identical to the same predicted by the van der Waals equation? (Hint, show that a volume of 3.43 L gives 101.3 kPa using the van der Waals equation for N_2).

Assume the temperature is a constant 25 °C. **(4 pts)**

4. I like martinis so let's work a partial volume question. Say I have a solution that is composed of water and ethanol. The density of the solution is 0.964 g/mL and I magically know that the partial molar volume of water at this concentration is 17.0 mL/mol and ethanol is 52.0 mL/mol. Tell me, what is the composition of the liquid by mass? **(7 pts)**

5. I need to make a solution of 50% ethanol in water (by mass). The partial molar volume of water is 17.0 mL/mol and the partial molar volume of ethanol is 52.0 mL/mol. What is the density of this solution? **(7 pts)**

6. A solution of methylbenzene (toluene) and dimethylbenzene (xylene) is as close to an ideal solution as you can get. What molar mixing ratio makes $\Delta_{mix}\mu$ the lowest possible? You might want to use a graphing calculator, and tell me what it is. **(5 pts)**

7. Given that water boils at 100 °C and has a heat of vaporization of 40.65 kJ/mol, what is the boiling point elevation for a saturated NaCl solution (40 g NaCl / 100 g H_2O)? Note, since NaCl will split into two species, so maybe the mole fraction of salt may not be all that easy to define… **(5.63 pts)**

8. If we didn't use the $\mathrm{T}\cdot\mathrm{T_{vap}} \approx \mathrm{T_{vap}^2}$ approximation in our derivation of the boiling point elevation equation we would have instead found: $\left(\mathrm{T}-\mathrm{T_{vap}}\right)=\frac{\chi_{\mathrm{salt}}\cdot\mathrm{R}\cdot\mathrm{T}\cdot\mathrm{T_{vap}}}{\Delta_{\mathrm{vap}}\mathrm{H_m}}$. Now solve for T using the example from question #7 and see whether you get closer to the experimental result of +8.7 °C. Hint: You will need to use a computer- we suggest Mathematica online: https://www.wolframalpha.com/. **(5 pts)**

9. a. If you never made the approximation $-\chi_{\mathrm{salt}} \approx \ln(1-\chi_{\mathrm{salt}})$ what would you have gotten for the boiling point of saturated water still using the equation above: $\left(\mathrm{T}-\mathrm{T_{vap}}\right)=\frac{\chi_{\mathrm{salt}}\cdot\mathrm{R}\cdot\mathrm{T}\cdot\mathrm{T_{vap}}}{\Delta_{\mathrm{vap}}\mathrm{H_m}}$? Hint: Part of the points if for showing how $\left(\mathrm{T}-\mathrm{T_{vap}}\right)=\frac{\chi_{\mathrm{salt}}\cdot\mathrm{R}\cdot\mathrm{T}\cdot\mathrm{T_{vap}}}{\Delta_{\mathrm{vap}}\mathrm{H_m}}$ should be adjusted without the natural log approximation. **(5 pts)**

b. It seems to me that using $\Delta_{\mathrm{vap}}\mathrm{H_m}$ = +40.65 kJ/mol is wrong since that is for pure water. What is the boiling point elevation of salt-saturated water if the vaporization enthalpy is actually $\Delta_{\mathrm{vap}}\mathrm{H_m}$ = +30.025 kJ/mol, of course using the "better" equation from pt. a? **(5 pts)**

10. Given that water melts at 0 °C and had a heat of fusion of +6.012 kJ/mol, what is the melting point for a saturated aqueous NaCl solution (35.7 g NaCl / 100 g H_2O)?

a. Use the simplified equation: $\Delta\mathrm{T}=\frac{\chi_{\mathrm{salt}}\cdot\mathrm{R}\cdot\mathrm{T_{fus}^2}}{\Delta_{\mathrm{fus}}\mathrm{H_m}}$. Note that the meaning of ΔT above is reversed from the boiling point elevation (#9a) because the temperature change is negative for freezing point depression. **(3 pts)**

b. Use an on-line solver (such as Wolfram alpha) to solve: $(\mathrm{T_{fus}}-\mathrm{T})=\frac{-\ln(1-\chi_{\mathrm{salt}})\cdot\mathrm{R}\cdot\mathrm{T}\cdot\mathrm{T_{fus}}}{\Delta_{\mathrm{fus}}\mathrm{H_m}}$. **(5 pts)**

Hint: the calculation in pt. a gives a positive ΔT, but you should know that this is the magnitude of how much less water freezes. Also, the experimental value of ΔT is 21 °C.

Problems: Theoretical or Explain in Words

1. If I mix two solvents together that form an ideal mixture, then I should calculate a negative $\Delta_{\mathrm{mix}}\mu$. Now let's say that the two solvents are the same thing. In this case, they obviously mix! However, $\Delta_{\mathrm{mix}}\mu = 0\ \mathrm{J/mol}$. Why is that given: $\Delta_{\mathrm{mix}}\mu=\mathrm{RT}\cdot\left(\chi_{\mathrm{A}}\ln(\chi_{\mathrm{A}})+\chi_{\mathrm{B}}\ln(\chi_{\mathrm{B}})\right)$? **(5 pts)**

Hint: this is the ideal equation and Raoults law is derived from: $\frac{P_A}{P_A^*}=\frac{\chi_A P_A^*}{P_A^*}=\chi_{\mathrm{A}}$.

2. I have a liquid A which has some partial pressure when in the pure state. I then added liquid B and, after equilibration, the partial pressure of A has not changed (no B vapor is detected). Did the liquids mix? **(3 pts)**

3. I don't mean to be dense, or maybe I do, but in question #2 above what would be a good physical reason for the fact that you can't detect the partial pressure of liquid B given that the partial pressure of A is unchanged? **(3 pts)**

4. Is it possible for two solutions to partially mix yet for you to still observe two distinct phases (i.e., can you still see a top layer and a bottom layer)? **(3 pts)**

5. The mixing entropy for two components A and B is:

$$\Delta_{\mathrm{mix}}\mathrm{S}=-\mathrm{nR}\sum\ln(\chi)=-\mathrm{nR}\cdot\left(\chi_{\mathrm{A}}\ln(\chi_{\mathrm{A}})+\chi_{\mathrm{B}}\ln(\chi_{\mathrm{B}})\right)=-\mathrm{nR}\cdot\left(\chi_{\mathrm{A}}\ln(\chi_{\mathrm{A}})+(1-\chi_{\mathrm{A}})\ln(1-\chi_{\mathrm{A}})\right)$$

If I simplify it a bit further I find: $\Delta_{\mathrm{mix}}\mathrm{S}=-\mathrm{nR}\cdot\left(\chi_{\mathrm{A}}\ln(\chi_{\mathrm{A}})+\ln(1-\chi_{\mathrm{A}})-\chi_{\mathrm{A}}\ln(1-\chi_{\mathrm{A}})\right)$.

What is the χ_{A} that maximizes the mixing entropy? **(10 pts)**

Hint: Think about how you leant to determine the maximum of a function. Also: $\frac{\partial \ln(x)}{\partial x} = \frac{1}{x}$, $\frac{\partial x\cdot\ln(x)}{\partial x} = 1 + \ln(x)$, $\frac{\partial \ln(1-x)}{\partial x} = \frac{-1}{1-x}$, and $\frac{\partial x\cdot\ln(1-x)}{\partial x} = \frac{-x}{1-x} + \ln(1-x)$. You should be able to whittle down the answer into the form: $\ln(x) - \ln(1-x) = 0$.

6. a. I have the following phenomenological model for excess enthalpy of mixing:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \sin(\pi\cdot\chi_A)\cdot(\alpha + \beta T)$$

Assume that the α and β parameters can have any unit, magnitude, or sign. Please state three things that are ***good*** about this model. **(3 pts)**

b. I have the following phenomenological model for excess enthalpy of mixing:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = \chi_A\cdot e^{\beta T}$$

Assume that the β parameter can have any unit, magnitude, or sign. Please state three things that are ***bad*** about this model. **(3 pts)**

7. Ideal solutions have negative $\Delta_{\mathrm{mix}}G = nRT\{\chi_A\ln(\chi_A) + \chi_B\ln(\chi_B)\}$ since $\Delta_{\mathrm{mix}}H = 0$ J and $\Delta_{\mathrm{mix}}S = -nR\{\chi_A\ln(\chi_A) + \chi_B\ln(\chi_B)\}$.

Let's derive a model for a non-ideal solution, whereby $\Delta_{\mathrm{mix}}U = 0$J, $\Delta_{\mathrm{mix}}V = \beta\cdot\chi_a\cdot\chi_b\cdot(nRT/P)$, and $\Delta_{\mathrm{mix}}S$ is the same as above. What do we derive for $\Delta_{\mathrm{mix}}G$ as a result? Hint: what is $\Delta_{\mathrm{mix}}H$? **(7 pts)**

8. When deriving the change in boiling point with the addition of salt, it must be true that the chemical potentials are equal: $\mu_{vapor} = \mu_{liquid}$ (note that we are assuming that the conditions are not the standard state, as water doesn't boil at 25 °C under 1 bar pressure). We can allow the chemical potential of the liquid to vary by the addition of salt via: $\mu_{liquid} \to \mu_{liquid} + RT\cdot\ln(\chi_{\mathrm{liq}})$, while we assume that the chemical potential of the vapor isn't changed by the addition of salt to the water. It is because we assume that the partial pressure of the vapor isn't changed.

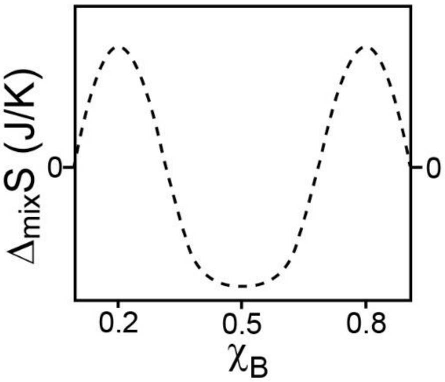
However, what if this isn't the case? Let's investigate this further by allowing the chemical potential of the vapor to change ala: $\mu_{vapor} \to \mu_{vapor} + \int_{P^*}^{P}\partial G_m = \mu_{vapor} + \int_{P^*}^{P}V_m\partial P$. This expression must be equal to $\mu_{liquid} + RT\cdot\ln(\chi_{\mathrm{liq}})$:

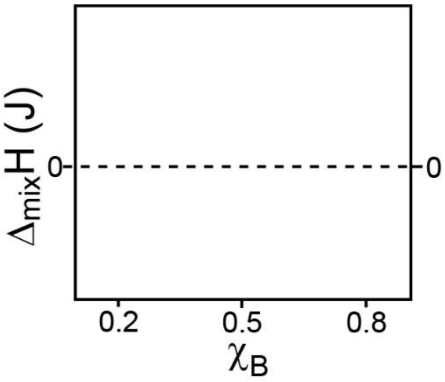
$$\mu_{vapor} + \int_{P^*}^{P}V_m\partial P = \mu_{liquid} + RT\cdot\ln(\chi_{\mathrm{liq}})$$

If we are talking about water and the temperature is near 100 °C, it is likely true that $\mu_{vapor} \approx \mu_{liquid}$. Using this approximation, can you derive an equation for the new vapor pressure (P above) starting with: $\int_{P^*}^{P}V_m\partial P = RT\cdot\ln(\chi_{\mathrm{liq}})$? Hint: if the vapor is a perfect gas then V_m = ? **(10 pts)**

9. There are two liquids, A and B, for which you have the following data concerning their mixing:

If you have 10 moles of A and 10 moles of B, what happens when they are added into a container? Your options are: 1) they mix fully, 2) they don't mix, 3) two or more mixed liquid phases form (if you think so, provide their exact compositions). Make sure you justify your answer! **(5 pts)**





10. Name two approximations that were used in the derivation of the equation for the freezing point depression: $\Delta T = \frac{\chi_{salt}\cdot R\cdot T_{fus}^2}{\Delta_{fus}H_m}$, which is why you were ~3 degrees off from the experimental value in number 10.a. of the previous section.

(6 pts)

Chapter 8: Phase Changes

Phase diagrams have shown up a few times throughout the earlier chapters (see Figure 1.2 on pg. 14 for example), and we will introduce them formally here. There are a multitude of potential phase diagram types that have different variables along the axes and may represent a single component or a solution. Shown in Figure 8.1 is a rather generic version of a P vs. T phase diagram for a single component. Understanding phase diagrams that are functions of pressure vs. temperature is a good way to start because these are intensive variables that define equilibrium. We also assume that a phase diagram represents a system 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 liquid water recorded is -45 °C![1,2]

There are a few parts of the phase diagram that bear discussion. For one, we see all the usual players- solid, liquid and gas, as well as a curious thing called “supercritical”. This is a phase that is like a combination of a liquid and a gas. There are broad regions for each phase, lines that delineate between them, and a single triple point between all three phases. There can be other triple points, although these occur in the solid phase region if we consider that solids can take different crystallographic structures; these are legitimate phases in their own right. There is of course only one gas and liquid phase, although helium can have two liquid phases due to some of the odd facet of quantum mechanics called a Bose-Einstein condensation. 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, so the application of high pressure inhibits the expansion of the solid into the liquid phase. There is one notable exception to this, which is water as it has a less dense solid phase. You know this already- because ice floats. As a result, the phase diagram of Figure 8.1

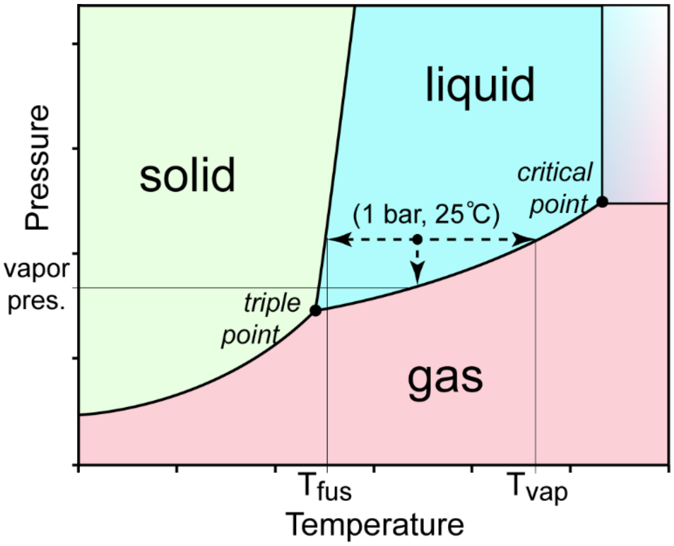


Figure 8.1. A typical P vs. T phase diagram. The lines guide the eye from the standard state to the melting and boiling points as well as the vapor pressure.

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, if we plot a point at 1 bar pressure at 25 °C in Figure 8.1 we see that this chemical is a liquid. Now, we make a line parallel to the x-axis, which is at a constant 1 bar pressure. From this line we can read off the melting point (T_{fus}) and boiling point (T_{vap}) where this line crosses the solid-liquid and liquid-vapor boundaries. What about that line that points straight down? The intersection of this line with the liquid-gas boundary provides the vapor pressure of the liquid as measured at 1 bar pressure, which allows us to determine the pure partial pressure of the vapor phase.

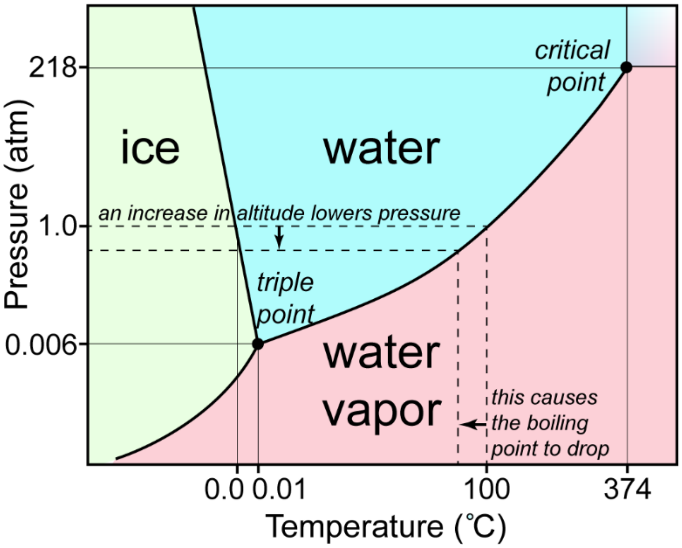


Figure 8.2. P vs. T phase diagram for water (axes are on a log scale). The data show that water boils at a lower temperature under lower atmospheric pressure.

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. 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 (in fact, water boils at 94.6 ºC in Albuquerque, New Mexico).

8.1 The Gibbs Phase Rule. In the following sections we will show how phase diagrams can be determined using thermodynamic relationships, so long as we have some experimental knowledge such as the location of a 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. 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 we read about in Chapter 2. Here we will define what we mean 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 water a few degrees and still have liquid water, even if we are at a higher or lower pressure altitude (i.e. Miami vs. Albuquerque).

Of course, if we keep heating the water eventually we reach a temperature where liquid water and steam co-exist (i.e. the water is boiling). Let's say at this point we desire the liquid to remain in equilibrium with the gas. If we change the temperature further then we also must change the pressure some particular amount, because if we don't then the system will fully collapse into either the liquid or gas state. This means that pressure is no longer a degree of freedom, because it is uniquely determined by the temperature necessary to maintain the liquid + gas equilibrium. Of course, we can also state that if we change the pressure then we don't have control over the temperature. In either case, we only have one degree of freedom if we are trying to maintain equilibrium between two phases.

Now we will put the discussion above 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: $f = 2$. Now we must consider that 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 2 more degrees of freedom. Thus, $f = 2 + c$. If there are multiple phases present, "p" in number, then we have even more degrees of freedom. For example, let's say that there is an ice cube in our ethanol + water mixture. We can decide how much ethanol and water should be added to the liquid and solid phases; this represents a total of $4 = c \cdot p$ degrees of freedom in addition to temperature and pressure. Consequently, $f = 2 + c \cdot p$.

However, we have run into a small problem. If we have a one phase system ($p = 1$) composed of two liquid components ($c = 2$), say ethanol and water, then is it true that we have 2 additional degrees of freedom aside pressure and temperature? Oddly no, because the system composition is characterized by only one variable, the mole fraction of water (χ_{water}). The mole fraction of the ethanol is automatically: $\chi_{EtOH} = 1 - \chi_{water}$. As a result, the presence of two components actually increases the degrees of freedom by 1. Again, let's use some mathematical representations to understand this better. Clearly if we have c components, then it must be true that the sum of their mole fractions is 1:

$$\chi_1 + \chi_2 + \chi_3 + \cdots \chi_c = 1$$

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:

$$\chi_1^{\alpha} + \chi_2^{\alpha} + \chi_3^{\alpha} + \cdots \chi_c^{\alpha} = 1$$
$$\chi_1^{\beta} + \chi_2^{\beta} + \chi_3^{\beta} + \cdots \chi_c^{\beta} = 1$$
$$\ldots$$
$$\chi_1^{p} + \chi_2^{p} + \chi_3^{p} + \cdots \chi_c^{p} = 1$$

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:

$$f = 2 + cp - p$$

There is a rule for this game: add the degrees of freedom to "f", but subtract the number of equal signs from constraining equations. Here is another- at equilibrium, the chemical potentials of the different components in the different phases must be equal as we showed in Ch. 6. For example, for water in equilibrium with ice it must be true that:

$$\mu^{\alpha} = \mu^{\beta}$$

(α=liquid, β=ice). This is another constraining equation, and we must make further reductions to the degrees of freedom as a result. And while it appears we have p such number of equal signs, however we have potentially additional phases from other components; in fact we have c of these equations for the various components:

$$\mu_1^{\alpha} = \mu_1^{\beta} = \cdots \mu_1^{p}$$
$$\mu_2^{\alpha} = \mu_2^{\beta} = \cdots \mu_2^{p}$$
$$\ldots$$
$$\mu_c^{\alpha} = \mu_c^{\beta} = \cdots \mu_c^{p}$$

The number of equal signs above, which represent losses of degrees of freedom, are $p - 1$ times the number of components: $c \cdot (p - 1)$. Thus we now have:

$$f = 2 + cp - p - c \cdot (p - 1)$$

A little algebra shows that:

$$f = 2 + c - p$$

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 diagram such as shown in Figure 8.1, only an open (or "flat") region can represent 2 degrees of freedom. In contrast, there is only: $f = 2 + c - p = 2 + 1 - 2 = 1$ degrees of freedom when representing two phases of a single component in equilibrium. 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 diagram 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; 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 because:

$$\partial G_m = \partial \mu = -S_m\,\partial T + V_m\,\partial P$$

As a result:

$$\left.\frac{\partial \mu}{\partial T}\right)_P = -S_m$$

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 for the simple reason that all chemicals are solids at very low temperatures. However, 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, we can use: $\partial G_m = \partial \mu = -S_m\,\partial T + V_m\,\partial P$

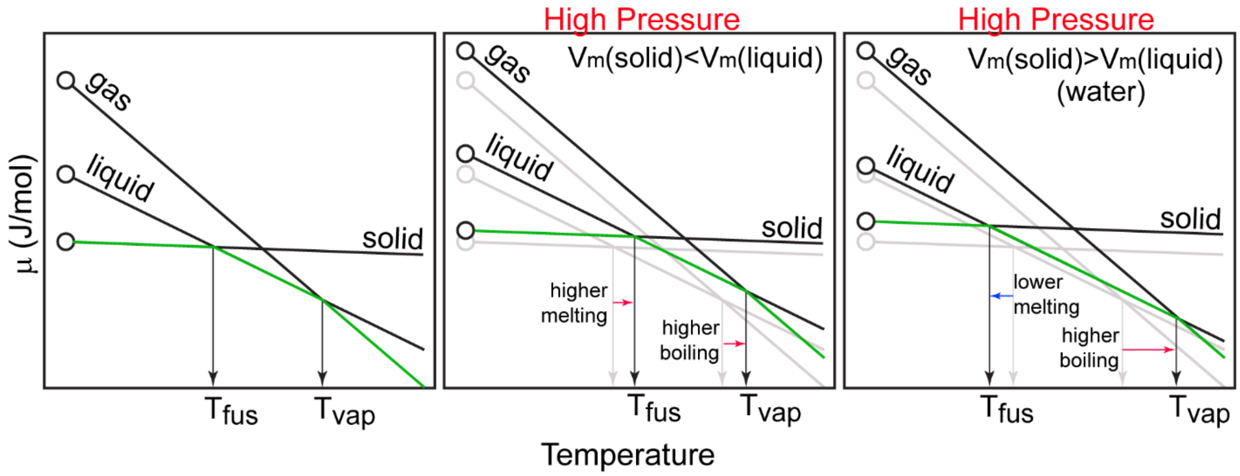


Figure 8.3. Chemical potential of three phases drops with increasing temperature. Higher pressure causes a rise in proportional to V_m. Materials like water thus have lower melting temperatures (T_{fus}) at higher pressure as a result.

to show that:

$$\left.\frac{\partial\mu}{\partial P}\right)_T = V_m$$

is always positive because volume per mole (the inverse of molar density) 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 (P, T) points of coexistance 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 any of the equations above for numerically calculating the boundaries in a phase diagram. This is because all these relationships involve absolute energies (i.e. G_m), but in practicality we must always use relative formation energies (i.e. $\Delta_f G_m$) when performing thermochemical calculations. Fortunately, we have two solutions to address this problem using the many tools discussed in Chapter 6. We can calculate temperature- and pressure-corrected chemical potentials $\mu(P, T) = \Delta_f G_m(P, T)$ for a solid, liquid and gas via:

$$\Delta_f G_m(P, T) = \Delta_f H_m(P, T) - T \times \Delta_f S_m(P, T)$$

where:

$$\Delta_f H_m(P, T) = \Delta_f H_m^{\circ} + \int_{298.15K}^{T} C_{P,m}(T)\,\partial T$$

and:

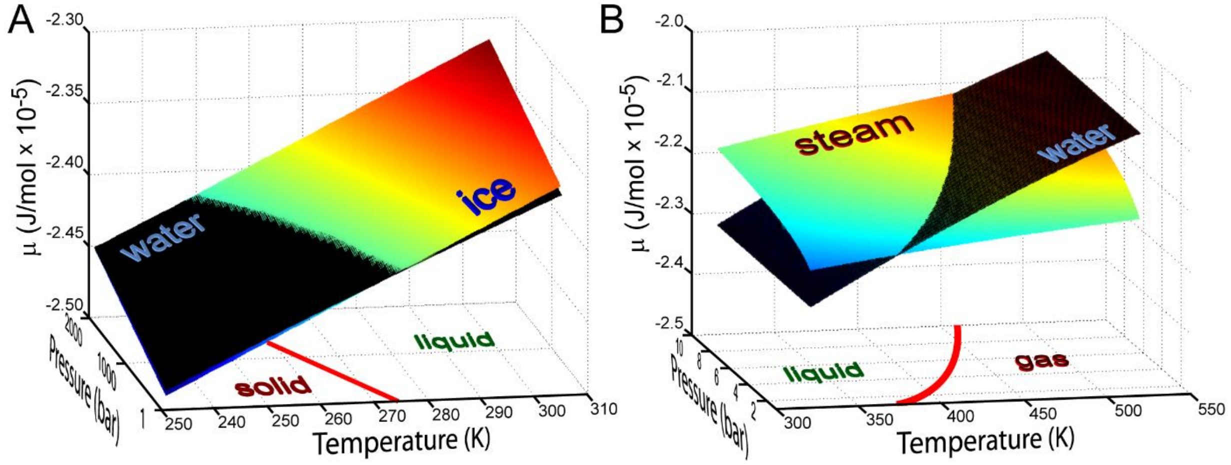


Figure 8.4. Calculating the chemical potential of various phases of water and plotting their crossing points defines the boundaries in a phase diagram.

$$\Delta_f S_m(P,T) = \Delta_f S_m^{\circ} + \int_{298.15K}^{T} \frac{C_P(T)}{T}\partial T - \int_{1bar}^{P} \frac{V_m}{T}\partial P$$

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 study phase boundaries using 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: $\mu^{\alpha} = \mu^{\beta}$. However, it is also true that the two phases must have equal changes in chemical potentials: $\partial\mu^{\alpha} = \partial\mu^{\beta}$ to be in equilibrium. Such small energy fluctuations can result from immeasurably small perturbations to the system, which remains stable due to this fact. 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:

$$V_m^{\alpha}\,\partial P - V_m^{\beta}\,\partial P = S_m^{\alpha}\,\partial T - S_m^{\beta}\,\partial T$$

Now we factor the change in pressure and temperature and divide the results:

$$\left(V_m^{\alpha} - V_m^{\beta}\right)\partial P = \left(S_m^{\alpha} - S_m^{\beta}\right)\partial T$$

$$\frac{\partial P}{\partial T} = \frac{\left(S_m^{\alpha} - S_m^{\beta}\right)}{\left(V_m^{\alpha} - V_m^{\beta}\right)} = \frac{\Delta S_m}{\Delta V_m}$$

Since we don't like to work with changes in entropy due to the complexity of entropy in general, we can make a clever substation. 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 then then substitute $\frac{\Delta H_m}{T}$ for ΔS_m to show:

$$\frac{\partial P}{\partial T} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T \cdot \Delta V_m}$$

This is the Clausius-Clapeyron equation, which dictates the effect of molar entropy and volume on the coexistence of different phases. Below, we use the Clausius-Clapeyron equation 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. First, we take the Clausius-Clapeyron relation and "juggle" the partials as so:

$$\partial P = \frac{\Delta_{fus} H_m}{\Delta_{fus} V_m} \cdot \frac{\partial T}{T}$$

At this point, we can easily integrate this equation using the enthalpy of fusion, which defines the change of solids melting as:

$$\Delta_{fus} H_m = \Delta_f H_{m,liquid} - \Delta_f H_{m,solid}$$

Likewise:

$$\Delta_{fus} V_m = V_{m,liquid} - V_{m,solid}$$

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 scenario, so we will approximate that this is not the case. 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 we will thus refer to the second state simply as (P, T):

$$P = \frac{\Delta_{fus}H_m}{\Delta_{fus}V_m} \cdot \ln\left(\frac{T}{T_t}\right) + P_t$$

The expression above gives us a formula for a line that delineates between the liquid and solid phases in a phase diagram.

There are a few points to consider. First, the input of energy (enthalpy) required to melt solids is usually rather large. At the same time, the difference in the densities of solids and liquids is very small. As a result, the $\frac{\Delta_{fus}H_m}{\Delta_{fus}V_m}$ ratio is huge. Coupled with the fact that natural logarithms are fairly linear, the relationship above is like a line with a very large slope. This is evident from the phase diagram in Figure 8.1, where you can see this behavior between the solid and liquid phases. Last, the slope should be positive, as $\Delta H_{m,fus}$ is always positive and the volume per mole of a liquid is generally greater than the volume per mole of a solid. This makes $\Delta V_{m,fus}$ likewise positive. 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. This is why the phase diagram of water has the solid-liquid line that slope to the left as seen in Figure 8.2.

8.2.1.2. Solid-Vapor. For the vapor phase in equilibrium with the solid, which we associate with the process of sublimation, we will manipulate the Clausius-Clapeyron relation as previously:

$$\partial P = \frac{\Delta_{sub}H_m}{T \cdot \Delta_{sub}V_m} \partial T$$

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 has a significant temperature dependence to its volume. 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. Now 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:

$$\ln(P) = \frac{-\Delta_{sub} H_m}{RT} + C$$

where the constant $C = \frac{\Delta H_{m,sub}}{RT_T} + \ln(P_t)$. If we cast this into a P vs. T diagram, we see that the relationship is like an exponential rise, which is how these appear in the examples seen in Figures 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 $C = \frac{\Delta H_{m,vap}}{RT_T} + \ln(P_t)$.

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 examples of phase changes exist. For example, there are two-dimensional phase changes that occur between soap molecules on the surface of water and phospholipids on the surfaces of living cells. Solid state materials have different magnetic phases, and biomolecules such as proteins undergo ordered / disordered phase changes. These can be observed by noting discontinuities with thermodynamic variables such as heat capacity upon heating, where energy is inputted with no observable change in temperature. Some examples of more interesting phase diagrams are discussed below.

8.3.1 Multicomponent Phase Diagrams, Pressure vs. composition. Mapping the phases of solutions is important for understanding many processes such as separation via distillation and how solder (i.e. wire glue) works. We will start with an ideal liquid solution from which vapors originate, where the liquid and vapor phases are charted as a function of pressure and solution mole fraction. First, we will make a plot of total pressure vs. liquid phase composition using Raoult's Law. However, Raolut's Law relates partial pressure of a component vs. that component's mole fraction: $P_B = \chi_B P_B^*$ for example. We must use this information to determine the net pressure, which we can do simply by noting that (for a 2 component solution)

$$P = P_A + P_B = \chi_A P_A^* + \chi_B P_B^*$$

Since $\chi_A = 1 - \chi_B$, $P = P_A + P_B = (1 - \chi_B)P_A^* + \chi_B P_B^*$, then:

$$P = P_A^* + \chi_B(P_B^* - P_A^*)$$

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 $\chi_B = \upsilon_B$? Not quite- this is because Raoult's Law relates a component's liquid mole fraction to its vapor

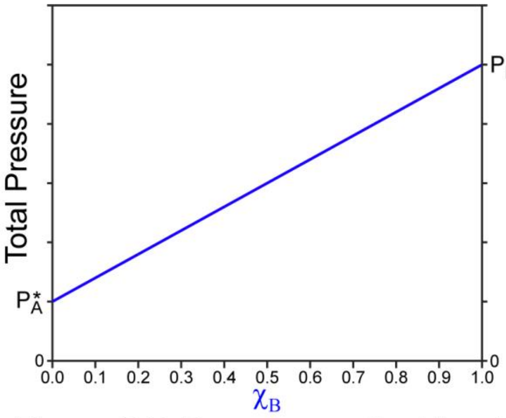


Figure 8.5. Pressure vs. liquid mole fraction.

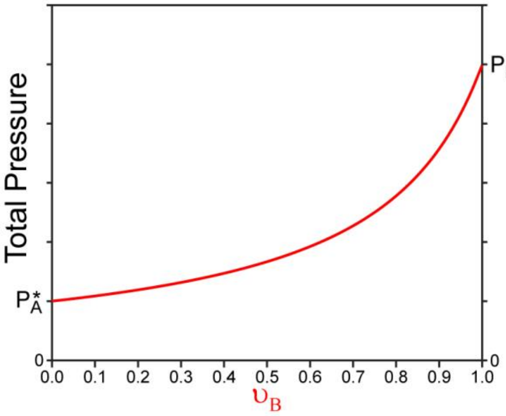


Figure 8.6. Pressure vs. vapor mole fraction.

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: $\mathrm{P_B} = \upsilon_\mathrm{B}\mathrm{P}$ which rearranges to:

$$\upsilon_\mathrm{B} = \frac{\mathrm{P_B}}{\mathrm{P}} = \frac{\mathrm{P_B}}{\mathrm{P_A^*} + \chi_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})} = \frac{\chi_\mathrm{B}\mathrm{P_B^*}}{\mathrm{P_A^*} + \chi_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})}$$

where we used the fact that $\mathrm{P} = \mathrm{P_A^*} + \chi_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})$ and $\mathrm{P_B} = \chi_\mathrm{B}\mathrm{P_B^*}$. A similar derivation for component "A" yields:

$$\upsilon_\mathrm{A} = \frac{\chi_\mathrm{A}\mathrm{P_A^*}}{\mathrm{P_B^*} + \chi_\mathrm{A}(\mathrm{P_A^*} - \mathrm{P_B^*})}$$

From here we see that, if $\mathrm{P_B^*} = \mathrm{P_A^*}$, then $\upsilon_\mathrm{B} = \chi_\mathrm{B}\frac{\mathrm{P_B^*}}{\mathrm{P_A^*}}$ and $\upsilon_\mathrm{A} = \chi_\mathrm{A}\frac{\mathrm{P_A^*}}{\mathrm{P_B^*}}$. 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 $\mathrm{P_B^*} \neq \mathrm{P_A^*}$.

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:

$$\chi_\mathrm{A} = \frac{\upsilon_\mathrm{A}\mathrm{P_B^*}}{\mathrm{P_A^*} - \upsilon_\mathrm{A}(\mathrm{P_A^*} - \mathrm{P_B^*})} = \frac{\upsilon_\mathrm{A}\mathrm{P_B^*}}{\mathrm{P_A^*} - (1 - \upsilon_\mathrm{B})(\mathrm{P_A^*} - \mathrm{P_B^*})} = \frac{\upsilon_\mathrm{A}\mathrm{P_B^*}}{\mathrm{P_B^*} - \upsilon_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})}$$

where we used $\upsilon_\mathrm{A} = (1 - \upsilon_\mathrm{B})$, and:

$$\chi_\mathrm{B} = \frac{\upsilon_\mathrm{B}\mathrm{P_A^*}}{\mathrm{P_B^*} - \upsilon_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})}$$

When we plug these into the expression for total pressure $\mathrm{P} = \mathrm{P_A} + \mathrm{P_B} = \chi_\mathrm{A}\mathrm{P_A^*} + \chi_\mathrm{B}\mathrm{P_B^*}$ we find:

$$\mathrm{P} = \frac{\upsilon_\mathrm{A}\mathrm{P_B^*}\mathrm{P_A^*}}{\mathrm{P_B^*} - \upsilon_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})} + \frac{\upsilon_\mathrm{B}\mathrm{P_B^*}\mathrm{P_A^*}}{\mathrm{P_B^*} - \upsilon_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})} = \frac{(\upsilon_\mathrm{A} + \upsilon_\mathrm{B})\mathrm{P_A^*}\mathrm{P_B^*}}{\mathrm{P_B^*} - \upsilon_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})} = \frac{\mathrm{P_A^*}\mathrm{P_B^*}}{\mathrm{P_B^*} - \upsilon_\mathrm{B}(\mathrm{P_B^*} - \mathrm{P_A^*})}$$

This behavior is illustrated in Figure 8.6 for the case of $\mathrm{P_B^*} \gg \mathrm{P_A^*}$.

Concerning multicomponent phase diagrams as shown in Figure 8.7, we now reveal the fact that these are actually two graphs that are superimposed, specifically Figures 8.5 and 8.6. As a result, the multicomponent phase diagram has two simultaneous x-axes, that being χ_B and υ_B in the example in Figure 8.7 Instead of a line between the liquid and vapor (gas) phase found in a single component phase diagram (Figures 8.1 & 8.2), we see instead a liquid + vapor region.

This is an area with two degrees of freedom, which is consistent with 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 $\chi_A = 0.4$). This is the "boring" part of the diagram, as opposed to point x_2 where we have two phases present. Each phase, liquid and vapor, has its own compositions that are determined by drawing tie lines to the left and right of the point to the liquid line (blue) and vapor line (red), respectively. 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" ($\chi_B = 0.33$, $\chi_A = 0.67$). At point x_3 the pressure is low enough such that both liquids have fully vaporized.

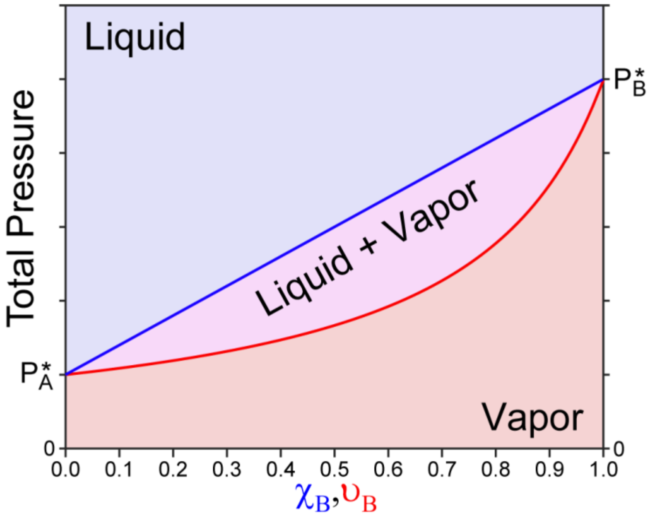


Figure 8.7. Multicomponent liquid-vapor phase diagram.

This diagram reveals that a liquid + vapor region exists because, at a given pressure, there is a composition of "A" and "B" that won't vaporize. For example, if we create a system at point x_1 and lower the pressure to x_2, then the components "A" and "B" vaporize (more so "B" and "A" due to the former's higher vapor pressure) until the liquid reaches an "A"-rich phase ($\chi_A = 0.67$ as discussed above). At this point, the liquid does not vaporize further. Consequently, the ability of the liquid composition to change gives it the degree of freedom to partially vaporize, which means that the liquid-vapor region are no longer phases

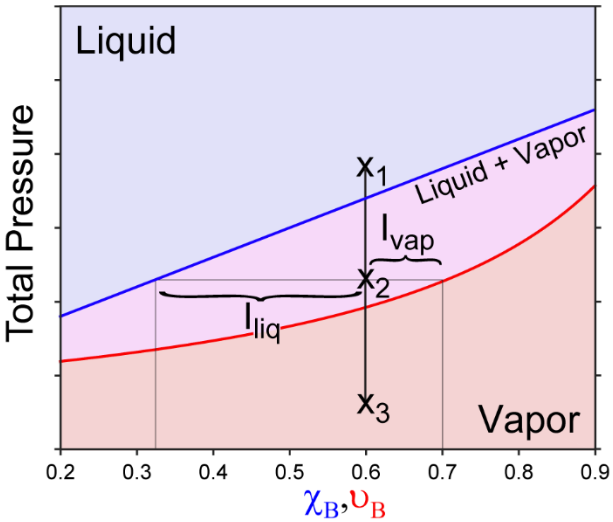


Figure 8.8. The lever rule for establishing compositions and relative quantities.

separated by a line but co-exist within a well-defined area.

8.3.1.1. The Lever Rule. The multicomponent phase diagrams in Figures 8.7 and 8.8 are more information rich than it appears and imparts an interesting lesson on degrees of freedom. Concerning the Gibbs Phase rule, 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 reach equilibrium- what 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 "B" or "A" isn't an available degree of freedom that can be used to alter the compositions of either the liquid or vapor phases. To demonstrate, note that at point x_2 we find that: $f = 2 + c - p = 2 + 2 - 2 = 2$. These two degrees of freedom are temperature and pressure. As a result, the addition of a small quantity of "B" doesn't fundamentally 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 where did the extra "B" go? The answer is that the excess "B" must be accounted for by an increase in the phase with more "B", which is the vapor. In other words, when you poured in more liquid "B" into the system, it reached equilibrium by creating more vapor that is rich in the "B" component while at the same time leaving 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 $\mathrm{I_{liq}}$ and $\mathrm{I_{vap}}$, then it is also true that the relative masses of liquid and vapor are related via:

$$\frac{\mathrm{I_{liq}}}{\mathrm{I_{vap}}} = \frac{\mathrm{m_{vap}}}{\mathrm{m_{liq}}}$$

where $\mathrm{m_{liq}}$ and $\mathrm{m_{vap}}$ 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 $\mathrm{I_{liq}}$, smaller $\mathrm{I_{vap}}$, and thus a greater amount of vapor. As in our discussion on single component phase diagrams, it appears that there is much greater information "hidden" in these diagrams than initially appears!

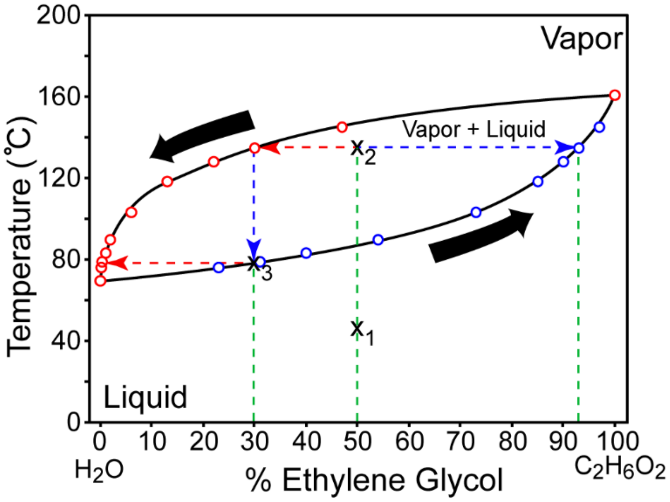


Figure 8.9. Multicomponent liquid-vapor phase diagram as a function of temperature.

8.3.1.2. Temperature vs. composition, azeotropes and distillation. The case of vapor-liquid phase diagrams. We can also demonstrate multicomponent phase diagrams as a function of temperature at constant pressure. In fact, these are more "practical" because they help us understand such processes as distillation as solid-state chemistry, as well as how circuit solder works. Shown in Figure 8.9 is a vapor-liquid T vs. χ_B diagram for a mixture of water and ethylene glycol at a pressure of 100 kPa (~1/3 an atm). There are a few simple observations, such as the fact that vapors are dominant at high temperatures while there is only one liquid phase at a low temperature. Also, the pure liquid boiling points are on the left and right sides of the graph, and we sensibly see that water's boiling point is lower than 100 °C given the reduced pressure.

Most importantly, the graph reveals the existence of a mixed phase state at intermediate temperatures and finite mole fractions. To read the graph we start at point x_1, which reveals that we have a liquid 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 ~93% ethylene glycol and a vapor that is ~30% water. The vapor and liquid are of course the same temperature, and the reason that the vapor has more water is clearly 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 so, as displayed on the graph as point x_3, then the vapor would early 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 the liquid phase as pure ethylene glycol once all the water vaporized out. Which is called distillation as implied in Figure 8.9.

Azeotropes are non-ideal liquid mixtures and have strikingly different behavior as shown in Figure 8.10. 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

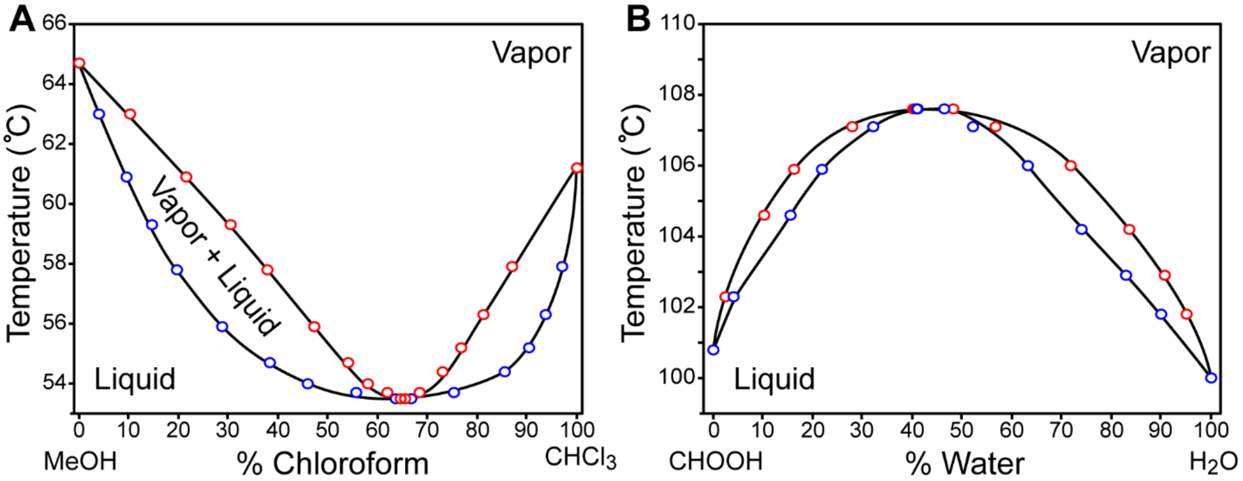


Figure 8.10. Azeotropes. **A.** A positive azeotrope has a lower boiling point than either constituent. Here, methanol and chloroform. **B.** A negative azeotrope composed of water and formic acid.

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 we have multicomponent phase diagrams for them as well as shown in Figure 8.11. For the most part, it is sensible to assume that liquids do not mix at lower temperature as shown in Figure 8.11 A for aniline in hexane. As such, if one had a 50%/50% mixture at a high temperature and cooled the solution, one would observe two phases form whereby one was rich in hexane (~70%) and the other with more aniline. Surprisingly, it is possible to observe the opposite- liquids that are mixed at a low temperature that separate upon

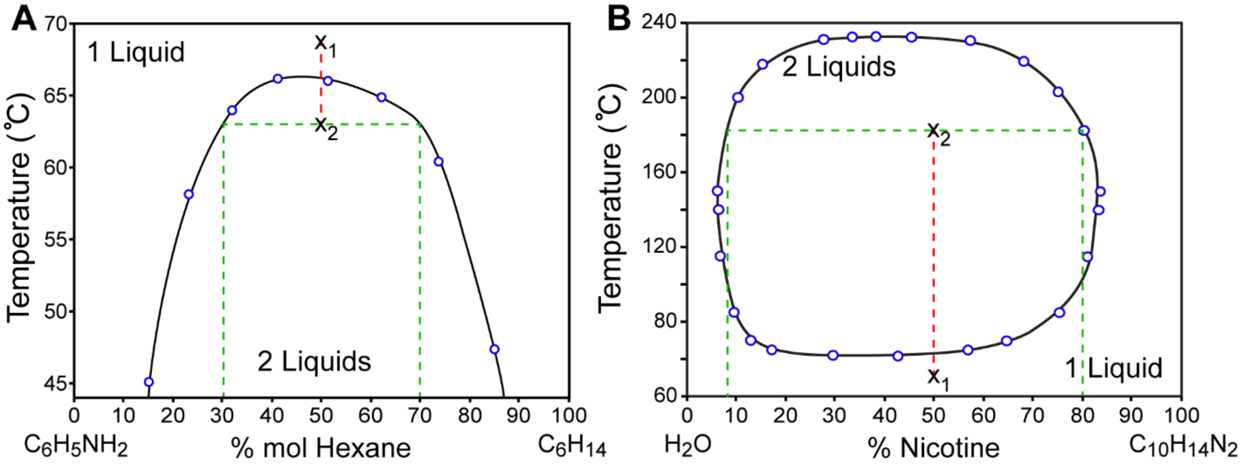


Figure 8.11. Liquid-liquid phase diagrams. **A.** A solution of aniline and hexane do not mix at low temperatures. **B.** A mixture of water and nictotine displays 2-phase behavior over a range of temperatures (pressure was not held constant and increased to ~20 atm at high T).

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 also exist to describe the solid state. Shown in Figure 8.11 A is the liquid-solid phase diagram of sodium and rubidium. Most of the phase diagram is intuitive; there is a single liquid phase at high temperature which solidifies the temperature is dropped enough. The crossover occurs at the melting point of sodium (97.8 C) on the left and rubidium (39.5 C) on the right.

To understand the in between spaces, lets start at point x_1 where we have a liquid composted of 40% Rb and 60% Na. If we cool to point x_2, what we observe is a liquid with solid pieces of sodium floating in it. The sodium is pure Na, while the liquid phase is correspondingly richer in Rb (60%). Upon further cooling to point x_3 we would have a solid mass, which contains phase segregated domains of sodium separated from rubidium. There is one other interesting feature in this figure, which is the “eutectic point” at -4.5 C at ~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 as well, whereby wires can be bonded to substrates using an alloy of 60% tin / 40% lead that melts at 190 °C that can be relatively safely created using a soldering iron.

Solid-solid phase diagrams can become extremely complex as shown in Figure 8.12 B, which is an example of a “reactive” phase diagram. The point x_1 describes a fully liquid system

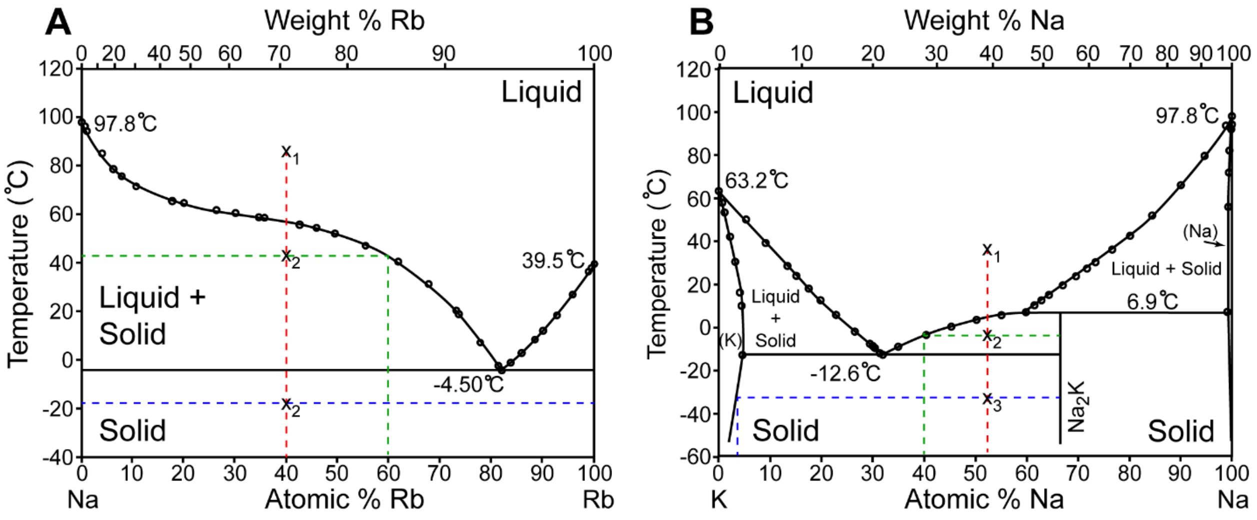


Figure 8.12. Liquid-Solid Phase Diagrams. **A.**Sodium-rubidium reveals a eutectic point at -4.5℃. **B.** The potassium-sodium diagram reveals the existance of a solid product, Na_2K.

that, upon cooling to point x_2 starts to exhibit solid particles floating in a more potassium-rich liquid. The solids are not pure metallic sodium, rather, Na_2K. This solid species continues to exist even as the liquid component solidifies upon cooling into a ~94% K / 6% Na alloy as seen at point x_3. The species Na_2K represents a distinct chemical entity than its constituents which is where the "reactive" label originates for such systems. These intermediates can have distinct properties, such as GaAs which is a semiconductor that forms from metallic Ga and As. The phase diagram in Figure 8.12 B also is an example of "incongruent melting", whereby Na_2K doesn't melt into that stoichiometry. Rather it loses its distinct chemical identity by melting into a form with solid sodium and leftover sodium-potassium liquid.

Conclusion.

References.

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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.

Problems: Numerical

1. The equation for the liquid-gas line is: $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{vap}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. At what temperature does H_2O boil given that the triple point is at T = 273.16 K and P = 611.73 Pa and $\Delta_{vap}H_m = 40.65$ kJ/mol? Hint: What do you use for P_2 to calculate T_2? **(6 pts)**

2. The equation for the solid-gas line is: $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{sub}H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$. At what temperature does CO_2 sublime at given that the triple point is at 216.6 K and 518.5 kPa and $\Delta_{sub}H_m = 25.2$ kJ/mol? Hint: What do you use for P_2 to calculate T_2? **(6 pts)**

3. Let's say that I have found an empirical equation for the sublimation of a gas, which is:
ln(P) = 21.15 – 3031/T, where T is in Kelvin and P is in Pascals.

a. How is it true the equation above is the exact same equation in question 2? **(3 pts)**

b. Is this material a gas or a solid at standard temperature? **(5 pts)**

4. Let's say that I have found an empirical equation for the boiling of a liquid, which is:
ln(P) = 24.32 – 4889.3/T, where T is in Kelvin and P is in Pascals.

a. How is it true the equation above is the exact same equation in question 1? **(3 pts)**

b. Is this material a gas or a liquid at standard temperature? **(5 pts)**

5. Let's say that I have found an empirical equation for the vapor pressure of a liquid over a certain temperature range. That equation is ln(P) = 24.36 - 4638/T, where T is in Kelvin and P is in Pascals. What is the enthalpy of vaporization?

6. I found an empirical equation for the vapor pressure of a substance is ln(P) = 24.63 - 4889.3/T, where T is in Kelvin and P is in Pascals. What is the enthalpy of vaporization? What is the boiling temperature? What is this mystery substance?

Problems: Theoretical or Explain in Words

1. At 100 °C water boils because $\mu_{vap} = \mu_{liq}$. If you salt it, the water stops boiling. Normally you raise the temperature (T) to get it boiling again so that the chemical potential of the vapor matches the chemical potential of the liquid:

$$\mu(T > 100\ °C)_{vap} = \mu(T > 100\ °C)_{liq} + RT \cdot \ln(\chi_{liq})$$

However, you could have also changed the pressure.

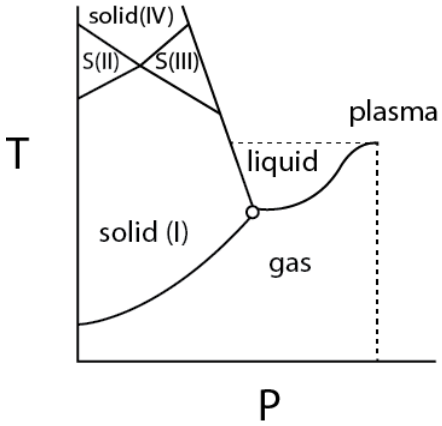
a. Best guess- should you raise or lower the exterior pressure to make the salted solution boil again at 100 °C? **(1 pt)**

b. Now let's do a derivation. If we keep the temperature at 100 °C but change the pressure, then the chemical potential equation is:

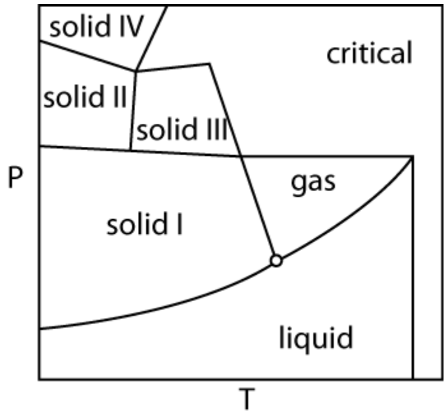
$$\mu(100\ °C)_{vap} + V_m\,\partial P = \mu(100\ °C)_{liq} + RT \cdot \ln(\chi_{liq})$$

You can solve the new boiling pressure by integrating the pressure-volume term as so: $\int_{1bar}^{P} V_m\,\partial P$ (use the perfect gas law!) where you solve for P_{final}. You need to know the relationship between $\mu(100\ °C)_{vap}$ and $\mu(100\ °C)_{liq}$! **(10 pts)**

2. I see four very wrong things happening in this phase diagram of a single substance. What are they, and why? **(8 pts)**



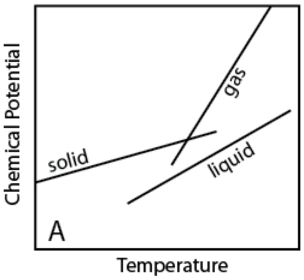
3. I see three very wrong things happening in this phase diagram of a single substance. What are they, and why? **(6 pts)**

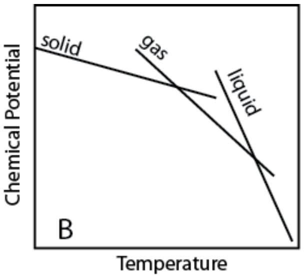


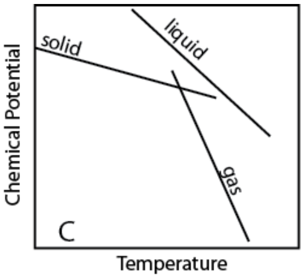
4. I show here 4 possible chemical potential diagrams vs. temperature for CO_2. FYI: CO_2 is called "dry ice" because as you allow the solid to warm to room temperature, it turns into a gas. **a.** Why do the lines slope downwards to begin with? **(5 pts)**

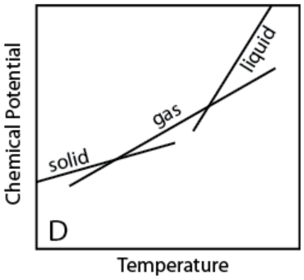
b. Which one is correct (A, B, C or D)? **(0 pts)**

c. Why did you see the answer as you did (basically what is wrong with the other 3)? **(5 pts)**







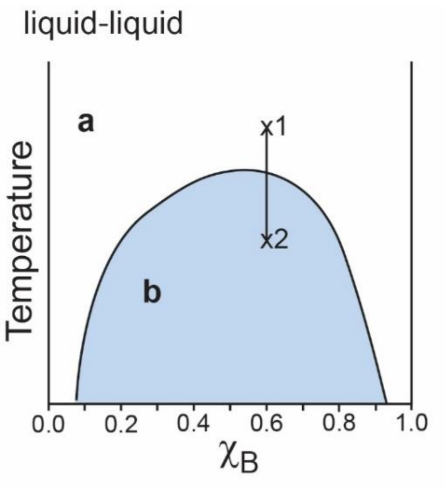


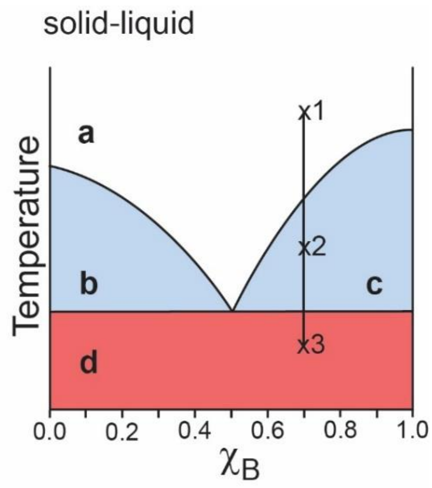
5. Here are some multi-component phase diagram questions that you should be able to figure out based on general principles. To work these questions:

1) determine where there is a single phase. Usually these are at extremes (low temperature = solids, low pressure = vapors).

2) Next, the remaining space are for two co-existing phases.

3) Connect a point to a phase boundary line right and left, and read-out the compositions on the x-axis.





LIQUID-LIQUID: a. What is (or are) in the regions (a) and (b)? **(4 pts)**

b. What is the compositions of the system at points x1 and x2 **(4 pts)**

SOLID-LIQUID: a. What is (or are) in the regions (a), (b)=(c), and (d)? **(6 pts)**

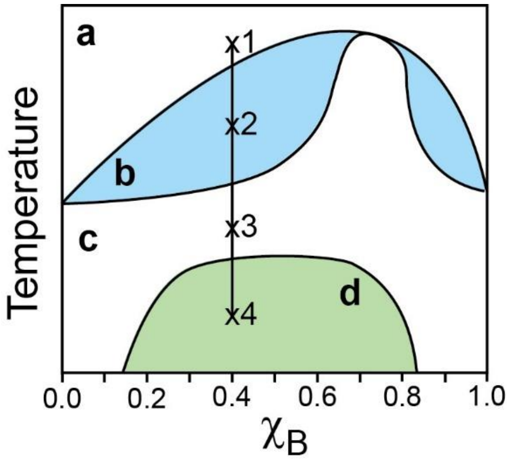
b. What is the compositions of the system at points x1, x2, and x3? **(6 pts)**

6. Given the following vapor-liquid-liquid phase diagram:

a. What are in regions a, b, c, and d? **(4 pts)**

b. What are the compositions and phases at points 1, 2, 3, and 4?

(4 pts)



Chapter 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 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 ~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 ~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:

$$U = N \cdot {}^{U_m}\!/_{N_A} + A \cdot \gamma$$

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

Example Problem 9.1

Problem: What percentage of atoms in a 100 μm cubic grain of salt resides on the surface? Note that this would be about the smallest sized object an average person can see.

Answer: The volume of the grain, times the density (2.16 g/cm^3) and divided by the mass of NaCl yields 3.7×10^{-8} mol, or 2.2×10^{16} NaCl units. With a surface area of 6×10^{-8} m^2 and a Na-Cl bond length of 0.236 nm, there are approximately 5.4×10^{11} NaCl units on the surface. Thus, the number atom ratio of surface to bulk atoms is 0.0024%.

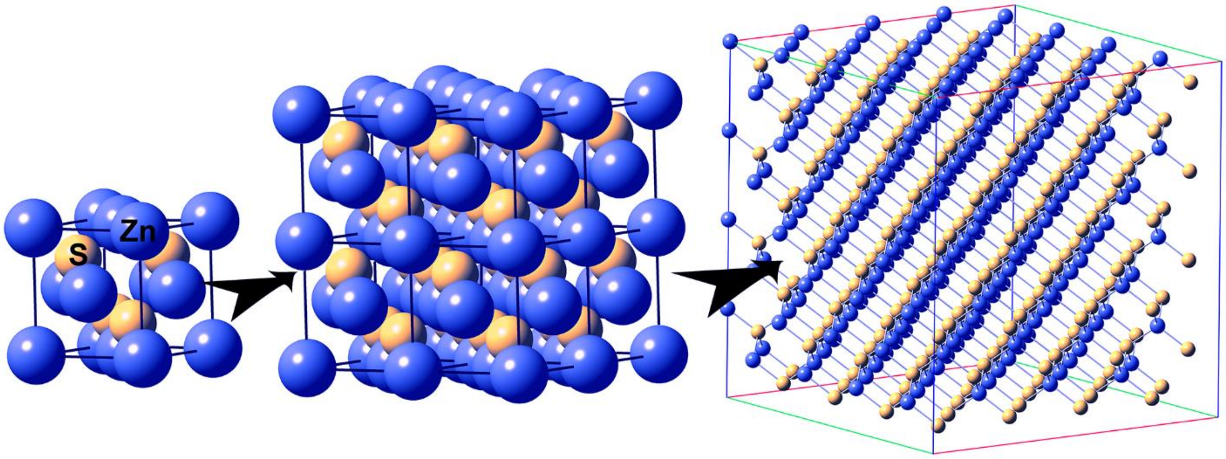


Figure 9.1. How a cubic unit cell (here, zinc sulfide or "zinc blende") is replicated into a bulk structure.

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

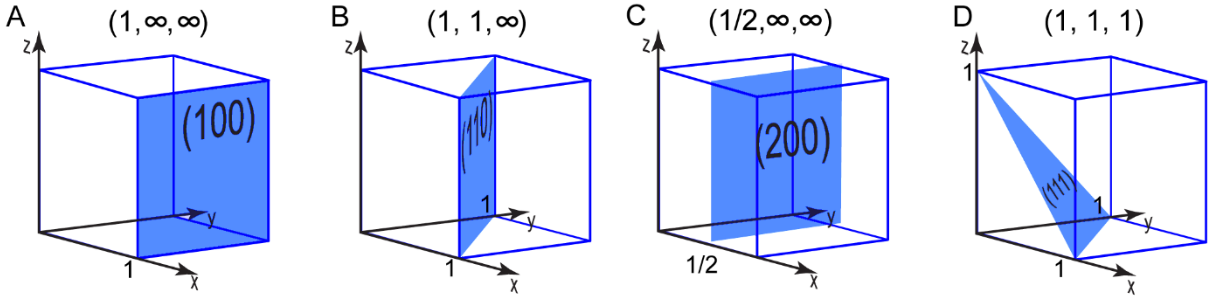


Figure 9.2. Miller indices are created by splicing planes (blue) through the unit cell. **A.** The plane bisects x at 1 and y, z at ∞. The resulting plane is the (1/1, 1/∞, 1/∞) = (1,0,0). **B.** The (1, 1, 0) plane. **C.** The (2, 0, 0) plane. **D.** The (1, 1, 1) plane.

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.

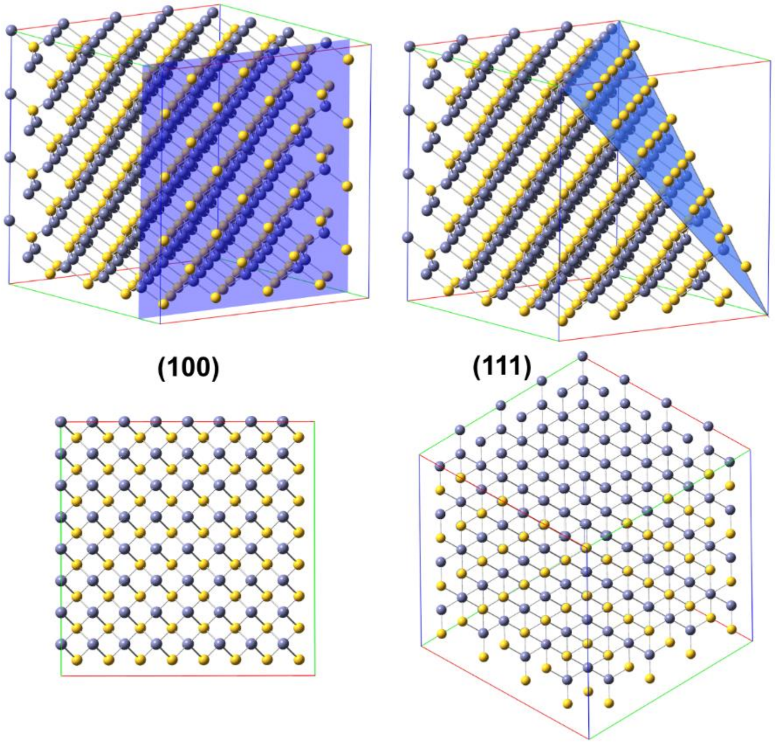


Figure 9.3 Viewing a material with a particular facet pointed directy up provides a unique represenation of the material.

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

Miller Planes, Surfaces and Directions

Miller indices can convey several properties of a material system, which is indicated by the notation used. Thus far we have used them to signify a surface using normal parentheses, as in (1 0 0). However, how different is (1 0 0) vs. (0 1 0)? While maybe the identity of the surface atoms are different, for the most part any combination of one "1" and two "0"s are all likely square-type surfaces. As such, we often refer to the {1 0 0} family of planes, which encompasses (1 0 0), (0 1 0) and (0 0 1). Miller indices also indicate direction, which is important in the growth of nanoparticles. For example, one can create rods of PbSe using colloidal chemistry, which grow in the [1 0 0] direction (note the square brackets). The direction is of course the vector that is normal to the (1 0 0) plane.

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 (1 0 0) vs. (1 1 1) surfaces of ZnS and NaCl.

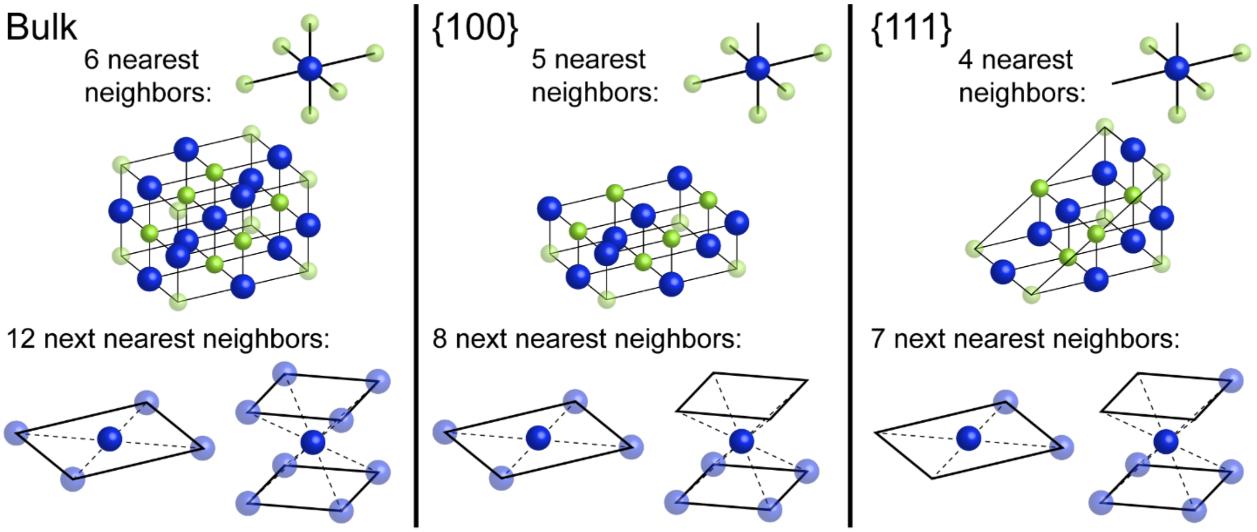


Figure 9.4. The number of bonds of an atom is reduced as a function of it's location on a surface.

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, γ, is exactly as described above. As for surface tension, σ, 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 (γ, J/m^2)
ZnS (100), Zn	1.12 [a]
ZnS (100), S	1.30 [a]
ZnS (111), Zn	0.87 [a]
ZnS (111), S	1.01 [a]
NaCl (100)	0.30
NaCl (110)	0.40

Liquid	σ, Surface Tension (mN/m)
Water (25 °C)	71.97
Mercury	487

Table 9.1 Surface energies and tension for various solids and liquids.

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:

$$\partial U = 0\text{ J} = T\,\partial S - P\,\partial V$$

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: $\partial U = 0\text{ J} = T\,\partial S + \gamma\,\partial\sigma$ 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 ~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

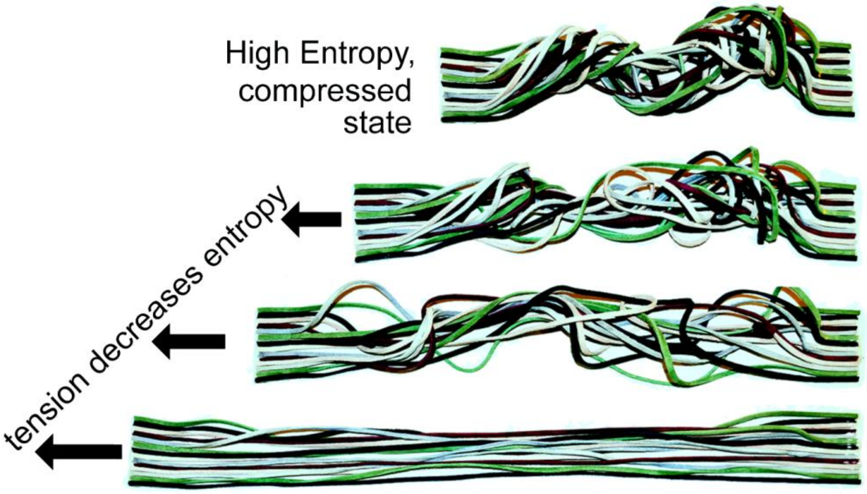


Figure 9.6. A rubber band is made of interconnected polymers. When contracted the polymers are all bunched together into a high entropy state. The opposite is true when stretched.

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 ~1 in. Therefore, heating shortens the rubber band, and while the effect is fairly slight, the shortening of the which is highly counterintuitive.

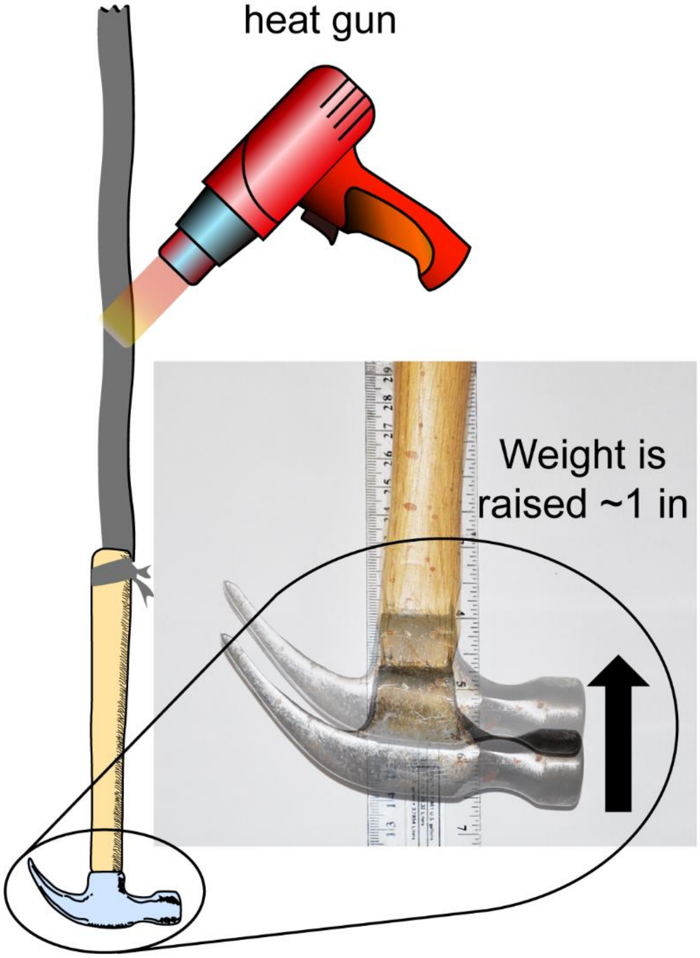


Figure 9.7. Heating a ~4 ft. elastic band raises a weight. This is due to an increase in entropy that accompanies greater tension.

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:

$$\partial \mathrm{w} = \gamma\, \partial \mathrm{A}$$

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 $\partial \mathrm{r}$. A sphere has a surface area $4\pi \mathrm{r}^2$, and a sphere with a radius $r + \partial \mathrm{r}$ has a surface area of:

$$4\pi(\mathrm{r} + \partial \mathrm{r})^2 = 4\pi \mathrm{r}^2 + 8\pi \mathrm{r} \cdot \partial \mathrm{r} + 4\pi(\partial \mathrm{r})^2$$

If we assume that $4\pi(\partial \mathrm{r})^2$ is very small compared to $8\pi \mathrm{r}\, \partial \mathrm{r}$ and can thus be ignored, then the change of surface area is:

$$\partial \mathrm{A} = 4\pi \mathrm{r}^2 + 8\pi \mathrm{r} \cdot \partial \mathrm{r} - 4\pi \mathrm{r}^2 = 8\pi \mathrm{r} \cdot \partial \mathrm{r}$$

Now when we insert this into the equation for work we find:

$$\partial \mathrm{w} = \gamma\,\partial \mathrm{A} = 8\pi\gamma \mathrm{r} \cdot \partial \mathrm{r}$$

As work is force times a change of distance and $\partial \mathrm{r}$ is that change of distance, then $8\pi\gamma\mathrm{r}$ 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:

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{8\pi\gamma\mathrm{r}}{4\pi\mathrm{r}^2} = \frac{2\gamma}{\mathrm{r}}$$

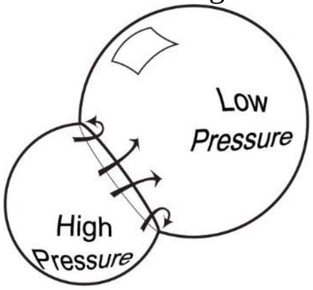
where again we use the fact that the area of a sphere is $4\pi\mathrm{r}^2$.

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:

$$\mathrm{P_{int}} = \mathrm{P} + \frac{2\gamma}{\mathrm{r}}$$

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: $\mathrm{P_{int}} = \mathrm{P} + \frac{4\gamma}{\mathrm{r}}$, 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:

$$\mu_{\mathrm{liq}} = \mu_{\mathrm{solid}}$$

However, we know that the solid nanoparticle has a higher internal pressure (P) compared to the bulk (P*) which raises its chemical potential: $\mu_{\mathrm{solid}} + \int \partial\mu_{\mathrm{solid}} = \mu_{\mathrm{solid}} + \int_{P^*}^{P} V_m^{\mathrm{solid}}\,\partial P$. 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:

$$\mu_{\mathrm{solid}} + \int_{T_{\mathrm{fus}}}^{T} -S_m^{\mathrm{solid}}\,\partial T + \int_{P^*}^{P} V_m^{\mathrm{solid}}\,\partial P$$

where $P > P^*$ and $T < T_{\mathrm{fus}}$. Concerning the surrounding liquid, it must experience the same decrease in temperature which also affects its chemical potential:

$$\mu_{\mathrm{liq}} + \int \partial\mu_{\mathrm{liq}} = \mu_{\mathrm{liq}} + \int_{T_{\mathrm{fus}}}^{T} -S_m^{\mathrm{liq}}\,\partial T$$

The temperature (T) can be found where chemical potentials of the solid nucleating nanoparticle and surrounding liquid remain equal:

$$\mu_{\mathrm{liq}} + \int_{T_{\mathrm{fus}}}^{T} -S_m^{\mathrm{liq}}\,\partial T = \mu_{\mathrm{solid}} + \int_{T_{\mathrm{fus}}}^{T} -S_m^{\mathrm{solid}}\,\partial T + \int_{P^*}^{P} V_m^{\mathrm{solid}}\,\partial P$$

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:

$$\int_{P^*}^{P} V_m^{\mathrm{solid}}\,\partial P \;= V_m^{\mathrm{solid}} \cdot \Delta P = V_m^{\mathrm{solid}} \cdot \frac{2\gamma}{r}$$

using the relationship $P_{\mathrm{int}} = P + \frac{2\gamma}{r}$ from section 9.1.1.

As for the effect of temperature, we combine the temperature integrals on the left side:

$$\mu_{\mathrm{liq}} - \mu_{\mathrm{solid}} + \int_{T_1}^{T_2} -S_m^{\mathrm{liq}}\,\partial T + \int_{T_{\mathrm{bulk}}}^{T} S_m^{\mathrm{solid}}\,\partial T = V_m^{\mathrm{solid}} \cdot \frac{2\gamma}{r}$$

and then combine them because they have the same limits:

$$\int_{T_{fus}}^{T} -S_m^{liq}\,\partial T + \int_{T_{fus}}^{T} S_m^{solid}\,\partial T = \int_{T_{fus}}^{T} \left(S_m^{solid} - S_m^{liq}\right)\partial T = \int_{T_{fus}}^{T} -\Delta S_{fus,m}\,\partial T = -\Delta S_{fus,m}(T - T_{fus})$$

Since we have already established that: $\mu_{liquid} - \mu_{solid} = 0\ J/mol$ we are left with:

$$-\Delta S_{fus,m}(T - T_{fus}) = V_m^{solid} \cdot \frac{2\gamma}{r}$$

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, $\Delta S_{fus,m} = \frac{\Delta H_{fus,m}}{T_{fus}}$:

$$T = T_{fus} - \frac{T_{fus} \cdot V_m^{solid}}{\Delta H_{fus}} \cdot \frac{2\gamma}{r}$$

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

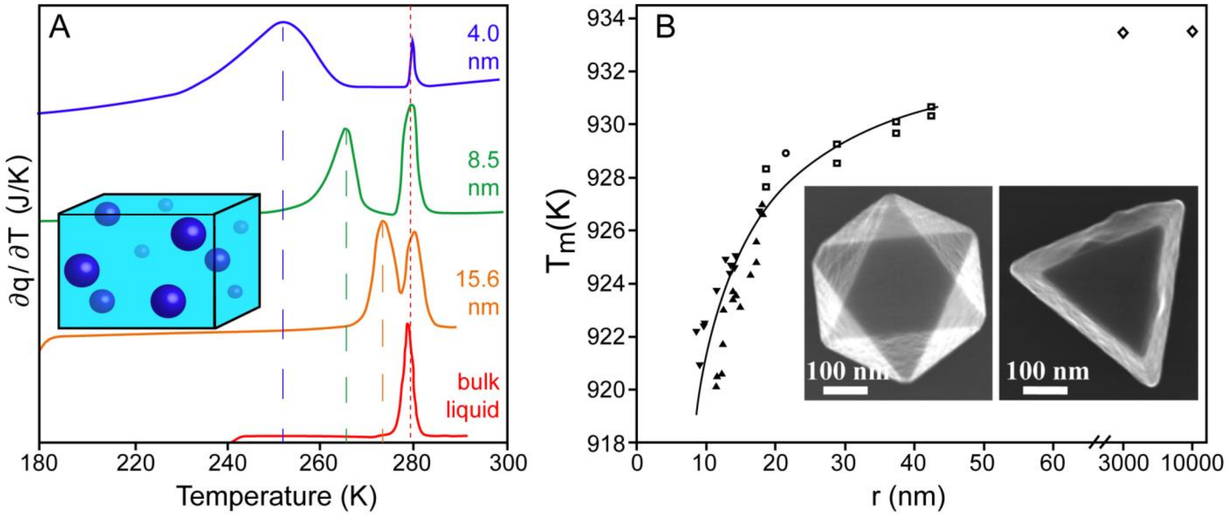


Figure 9.9. A. Differential Scanning Calorimetry on controlled pore glass filled with benzene reveals lower temperature melting points for the solvent confined in smaller volume pores. A bulk component is observed in the samples. **B.** Melting temperature of various sized Al nanoparticles that can be chemically synthesized using colloidal chemistry.

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:

$$\mathrm{V_m^{liq}} \cdot \partial \mathrm{P^{liq}} + \mathrm{S_m^{liq}} \cdot \partial \mathrm{T} = \mathrm{V_m^{vap}} \cdot \partial \mathrm{P} + \mathrm{S_m^{vap}} \cdot \partial \mathrm{T}$$

where the changes in pressure of the liquid $\partial \mathrm{P^{liq}}$ is not the same as the gas $\partial \mathrm{P}$ 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 $\partial \mathrm{T} = 0$ K. We are left with:

$$\mathrm{V_m^{liq}}\, \partial \mathrm{P^{liq}} = \mathrm{V_m^{vap}}\, \partial \mathrm{P}$$

Now consider how the relationship would change as a function of changing radius. Since the liquid phase is in the interior of the droplet:

$$\partial \mathrm{P^{liq}} = \partial \left(\mathrm{P} + \frac{2\gamma}{\mathrm{r}} \right) = \partial \mathrm{P} + 2\gamma \cdot \partial \left(\frac{1}{\mathrm{r}} \right)$$

Plugging this into $\mathrm{V_m^{liq}}\, \partial \mathrm{P^{liq}} = \mathrm{V_m^{vap}}\, \partial \mathrm{P}$ from above along with some simplification:

$$\partial \mathrm{P} + 2\gamma \cdot \partial \left(\frac{1}{\mathrm{r}} \right) = \frac{\mathrm{V_m^{vap}}}{\mathrm{V_m^{liq}}} \partial \mathrm{P}$$

Now we will bring $\partial \mathrm{P}$ over to one side and $2\gamma \cdot \partial \left(\frac{1}{\mathrm{r}} \right)$ to the other:

$$\partial \mathrm{P} - \frac{\mathrm{V_m^{vap}}}{\mathrm{V_m^{liq}}} \partial \mathrm{P} = \left(\frac{\mathrm{V_m^{liq}}}{\mathrm{V_m^{liq}}} - \frac{\mathrm{V_m^{vap}}}{\mathrm{V_m^{liq}}} \right) \partial \mathrm{P} = -\left(\frac{\mathrm{V_m^{vap}} - \mathrm{V_m^{liq}}}{\mathrm{V_m^{liq}}} \right) \partial \mathrm{P} = -2\gamma \cdot \partial \left(\frac{1}{\mathrm{r}} \right)$$

Thus:

$$\frac{\mathrm{V_m^{vap}} - \mathrm{V_m^{liq}}}{\mathrm{V_m^{liq}}} \partial \mathrm{P} = 2\gamma \cdot \partial \left(\frac{1}{\mathrm{r}} \right)$$

Now we assume that the volume of the vapor is much higher than the liquid $\mathrm{V_m^{vap}} - \mathrm{V_m^{liq}} \approx \mathrm{V_m^{vap}}$, and we will turn to our old friend the perfect gas law: $\mathrm{V_m^{vap}} \approx \frac{\mathrm{RT}}{\mathrm{P}}$. Thus:

$$2\gamma \cdot \partial \left(\frac{1}{\mathrm{r}} \right) = \frac{\mathrm{RT}}{\mathrm{V_m^{liq}}} \frac{\partial \mathrm{P}}{\mathrm{P}}$$

Integration of both sides yields:

$$\int_{0\ \mathrm{m}^{-1}}^{1/\mathrm{r}} 2\gamma \cdot \partial\left(\frac{1}{\mathrm{r}}\right) = \int_{\mathrm{P}^*}^{\mathrm{P}} \frac{\mathrm{RT}}{\mathrm{V}_\mathrm{m}^\mathrm{liq}} \frac{\partial \mathrm{P}^\mathrm{vap}}{\mathrm{P}}$$

where P* is the pure partial pressure. The left side is: $\int_{0\ \mathrm{m}^{-1}}^{1/\mathrm{r}} 2\gamma \cdot \partial\left(\frac{1}{\mathrm{r}}\right) = 2\gamma \cdot \frac{1}{\mathrm{r}}$ and the right is: $\frac{\mathrm{RT}}{\mathrm{V}_\mathrm{m}^\mathrm{liq}} \ln\left(\frac{\mathrm{P}}{\mathrm{P}^*}\right)$. Equating the two: $\frac{\mathrm{RT}}{\mathrm{V}_\mathrm{m}^\mathrm{liq}} \ln\left(\frac{\mathrm{P}}{\mathrm{P}^*}\right) = 2\gamma \cdot \frac{1}{\mathrm{r}}$ yields the Kelvin equation:

$$\ln\left(\frac{\mathrm{P}}{\mathrm{P}^*}\right) = \frac{2\gamma \mathrm{V}_\mathrm{m}^\mathrm{liq}}{\mathrm{RT}} \cdot \frac{1}{\mathrm{r}}$$

And thus $\mathrm{P} = \mathrm{P}^* \cdot \exp\left(\frac{2\gamma \mathrm{V}_\mathrm{m}^\mathrm{liq}}{\mathrm{RT}} \cdot \frac{1}{\mathrm{r}}\right)$. 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:

$$\frac{2\gamma \mathrm{V}_\mathrm{m}^\mathrm{liq}}{\mathrm{RT}} = \frac{\mathrm{J/m^2 \cdot m^3/mol}}{\mathrm{J/K/mol \cdot K}} = \mathrm{meters}$$

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 $\frac{2\gamma \mathrm{V}_\mathrm{m}^\mathrm{liq}}{\mathrm{RT}}$ is often described as a critical radius R_crit, which allows us to demonstrate the Ostwald-Freulich equation:

$$\mathrm{P} = \mathrm{P}^* \cdot e^{\frac{\mathrm{R}_\mathrm{crit}}{\mathrm{r}}}$$

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:

$$\Delta\mathrm{G} = 4\pi \cdot \gamma \cdot \mathrm{r}^2 - \frac{4}{3}\pi \cdot \mathrm{r}^3 \cdot |\Delta_\mathrm{f}\mathrm{G}_\mathrm{V}|$$

where γ is the surface energy and $|\Delta_\mathrm{f}\mathrm{G}_\mathrm{V}|$ 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. The Nernst equation…

Voltage, Coulombs, electromotive force, etc.

9.3.1 Battery Design. 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. The overall reaction and potential for a Cu^{2+} / Cu^{+} cell given the following:

Rxn	E° (V)
$Cu^{2+}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)}$	0.340
$Cu^{+}_{(aq)} + e^{-} \rightarrow Cu_{(s)}$	0.522

Make sure you show how to determine the potential by adding ΔG's.

References

[1]
[2]
[3] 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.

Problems: Numerical

1. I am trying to build a battery based of the following chemical reactions:
$A_{(s)} \rightarrow 2\,e^- + A_{(aq)}^{2+}$
$B_{(aq)}^{2+} + 2\,e^- \rightarrow B_{(s)}$
If the net reaction has a ΔG_m of −100 kJ/mol, what is the standard electromotive force (i.e. voltage) for the reaction? **(4 pts)**

2. You work in a battery production plant and decide to make devices from chemicals “A” and “B”. Here are their standard reduction potentials:

Rxn	E° (V)
$A_{(aq)}^{1+} + 1\,e^- \rightarrow A_{(s)}$	−2.0
$B_{(aq)}^{2+} + 2\,e^- \rightarrow B_{(s)}$	−2.0

a. Let’s say that the “dominant” reaction is the 1st one (the “A” reaction, which of course is spontaneous in reverse). When you conform the 2nd reaction to it, what is the resulting voltage of the electrochemical cell? **(4 pts)**
b. Let’s say that the “dominant” reaction is the 2nd one (the “B” reaction, which of course is spontaneous in reverse). When you conform the 1st reaction to it, what is the resulting voltage of the electrochemical cell? **(4 pts)**

3. Given the following:

Rxn	E° (V)
$A_{(s)} \rightarrow 2\,e^- + A_{(aq)}^{2+}$	1.0
$B_{(aq)}^{3+} + 3\,e^- \rightarrow B_{(s)}$	2.0

We can see that the “dominant” reaction is the 2nd “B” one because it has the most positive voltage E°, which is equivalent to the most negative chemical potential.
a. However, we have run into a problem- how do we write the stoichiometry of the reaction? Since the “B” reaction has the most negative $\Delta_{rxn}G_m^{\circ}$, we will force the first reaction to conform to the second in terms of balancing electrons:

Rxn	E° (V)
$B_{(aq)}^{3+} + 3\,e^- \rightarrow B_{(s)}$	2.0
$3/2\ A_{(s)} \rightarrow 3\,e^- + 3/2\ A_{(aq)}^{2+}$	1.0

What is the potential of this cell as calculated by the sum of the individual ΔG’s and converted back to voltage via the Nernst equation? **(5 pts)**

b. Now we could have simply matched the stoichiometry of the electrons as below to try to avoid having 3/2 an “A” atom:

Rxn	E° (V)
$2\,B_{(aq)}^{3+} + 6\,e^- \rightarrow 2\,B_{(s)}$	2.0
$3\,A_{(s)} \rightarrow 6\,e^- + 3\,A_{(aq)}^{2+}$	1.0

What is the potential of this cell as calculated by the sum of the individual ΔG’s and converted back to voltage via the Nernst equation? **(5 pts)**

4. Here are two half-reactions with EMF’s:
$2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2(g)}$ E° = 0.0 V
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$ E° = −2.71 V

a. Tell me how to correctly designate the operation of the battery, i.e., is it:
$2\,H^+_{(aq)} + 2\,Na_{(s)} \rightarrow H_{2(g)} + 2\,Na^{2+}_{(aq)}$
or:
$H_{2(g)} + 2\,Na^{2+}_{(aq)} \rightarrow 2\,H^+_{(aq)} + 2Na_{(s)}$
and why! **(4 pts)**
b. Why does this: $2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2(g)}$ have an E° = 0.0 V? **(2 pts)**
(hint: for pt. b you might want to watch the video since you’re constantly skipping class)

5. What is the overall reaction and potential for a battery composed of the two half reactions:

Rxn		E° (V)
$N_{2(g)} + 4H_2O + 2e^-$	$\rightarrow 2NH_2OH_{(aq)} + 2OH^-$	−3.04
$Na^+_{(aq)} + e^-$	$\rightarrow Na_{(s)}$	−2.71

(10 pts)

Make sure you show how to determine the potential by adding ΔG's.

6. What is the overall reaction and potential for a battery composed of the two half reactions:

Rxn		E°
$Si_{(s)} + 4\,H^+ + 2\,e^-$	$\rightarrow SiH_{4(g)}$	−0.14V
$Ag^+_{(aq)} + e^-$	$\rightarrow Ag_{(s)}$	0.80V

(10 pts)

Make sure you show how to determine the potential by adding ΔG's.

Problems: Theoretical or Explain in Words

1. Joule's experiment involved expanding a gas into a vacuum under adiabatic conditions, thus there is no heat and no work making ΔU = 0 J. Now let's do the same for a rubber band that is being stretched under adiabatic conditions, where the change in internal energy is:

$$\partial U = \partial q + \partial w = 0 + f\,\partial L = f\,\partial L$$

Here, f is tension and L is the length of the rubber band.

a. What are the units of f? **(2 pts)**

b. How would you make the work part 0 J to repeat the Joule experiment with a rubber band instead of a gas? **(3 pts)**

Hint for pt. b, if the rubber band has tension (i.e. a finite f), it's because you are stretching it.

For now, let's prove that the differential of pressure $\partial P(V,T) = \frac{n\cdot R}{V}\cdot\partial T$ is exact, starting with the Euler test: $\frac{\partial}{\partial V}\frac{\partial P}{\partial T}\Big)_V\Big)_T = \frac{\partial}{\partial T}\frac{\partial P}{\partial V}\Big)_T\Big)_V$. We insert $\frac{n\cdot R}{V}\cdot\partial T$ for ∂P:

$$\frac{\partial}{\partial V}\frac{n\cdot R}{V}\frac{\partial T}{\partial T}\Big)_V\Big)_T = \frac{\partial}{\partial T}\frac{n\cdot R}{V}\frac{\partial T}{\partial V}\Big)_T\Big)_V$$

First, $\frac{\partial T}{\partial T}\Big)_V = 1$. Next, we simplify Here we employ the fact that $PV = nRT$, and thus (left side): $n\cdot R\cdot\frac{\partial T}{\partial P}\Big)_V = n\cdot R\cdot\frac{V}{n\cdot R} = V$ and likewise on the right: $n\cdot R\cdot\frac{\partial T}{\partial V}\Big)_P = n\cdot R\cdot\frac{P}{n\cdot R} = P$. We are left with:

$$\frac{\partial V}{\partial V}\Big)_P = \frac{\partial P}{\partial P}\Big)_V$$

$$1 = 1$$

So, $n\cdot R\cdot\partial T$ is an exact differential. As we shall see, state functions (U, S, A, H, G) are exact, while ∂work and ∂heat are inexact.

Chapter 10. Kinetic Theory of Gases

When studying the world we measure inputs that originate from single molecules. However, our eyes and ears and ~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:

	Coin 1	**Coin 2**
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: $0.25 = 0.5 \times 0.5$. 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	~0%

Table 10.1. The probability of observing an even split from a large number of coins is low. 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 ~8% chance of observing exactly 50 heads and 50 tails. However, the odds of observing 50 ± 3 heads, i.e. between 47 → 53, are ~52%. Likewise, if we ping 1000 molecules the probability is ~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: $\mathrm{P} = \mathrm{P}_{\mathrm{dens}}(\mathrm{y}) \cdot \Delta\mathrm{y}$ to redefine the probability. Here, P is the probability we are familiar with, $\Delta\mathrm{y}$ is the spread, and $\mathrm{P}_{\mathrm{dens}}(\mathrm{y})$ 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 ± 30 heads the answer is ~50%. Thus, when we ask the right questions, we regain the ability to discern the fact that the coin molecules have two even sides!

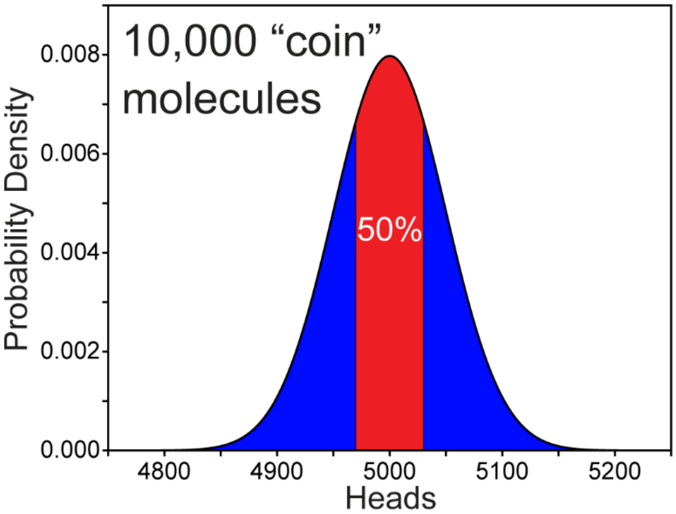


Figure 10.1. Histogram of the probability density for the total number of "heads" when observing a population of 10,000.

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 $\Delta\mathrm{y} \rightarrow \partial\mathrm{y}$, which makes our expression for probability:

$$\mathrm{P} = \mathrm{P}_{\mathrm{dens}}(\mathrm{y}) \cdot \Delta\mathrm{y} \rightarrow \mathrm{P}_{\mathrm{dens}}(\mathrm{y}) \cdot \partial\mathrm{y}$$

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 $\mathrm{P}_{\mathrm{dens}}(\mathrm{y})$ has inverse units of the property **y** that is under investigation. Second, a partial is technically infinitely small, so the value of $\partial\mathrm{y}$ 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 $\mathrm{E_i}$. The probability that a molecule has exactly $\mathrm{E_i}$ of kinetic energy is: $\mathrm{P(E_i) = P_{dens}(E_i) \cdot \partial E = 0\%}$, 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: $\int_{0\,\mathrm{J}}^{\infty\,\mathrm{J}} \mathrm{P_{dens}(E) \cdot \partial E = 1.0}$. 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:

$$\int_{lower\ limit}^{upper\ limit} \mathrm{P_{dens}(y) \cdot \partial y = 1.0}$$

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: $<\mathrm{E}>$. Probability distribution are both useful and often necessary for determining as much, and the correct calculus expression is: $<\mathrm{E}>= \int_{0\,\mathrm{J}}^{\infty\,\mathrm{J}} \mathrm{E \cdot P_{dens}(E) \cdot \partial E}$ where you integrate the thing you want the average of times its probability distribution over all possible values. In general, for any property **y**:

$$<\mathrm{y}>= \int_{lower\ limit}^{upper\ limit} \mathrm{y \cdot P_{dens}(y) \cdot \partial y}$$

What is more interesting is that you can also determine what are called higher "moments", such as the 2nd moment (the average of the square) of property **y**:

$$<\mathrm{y^2}>= \int_{lower\ limit}^{upper\ limit} \mathrm{y^2 \cdot P_{dens}(y) \cdot \partial y}$$

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:

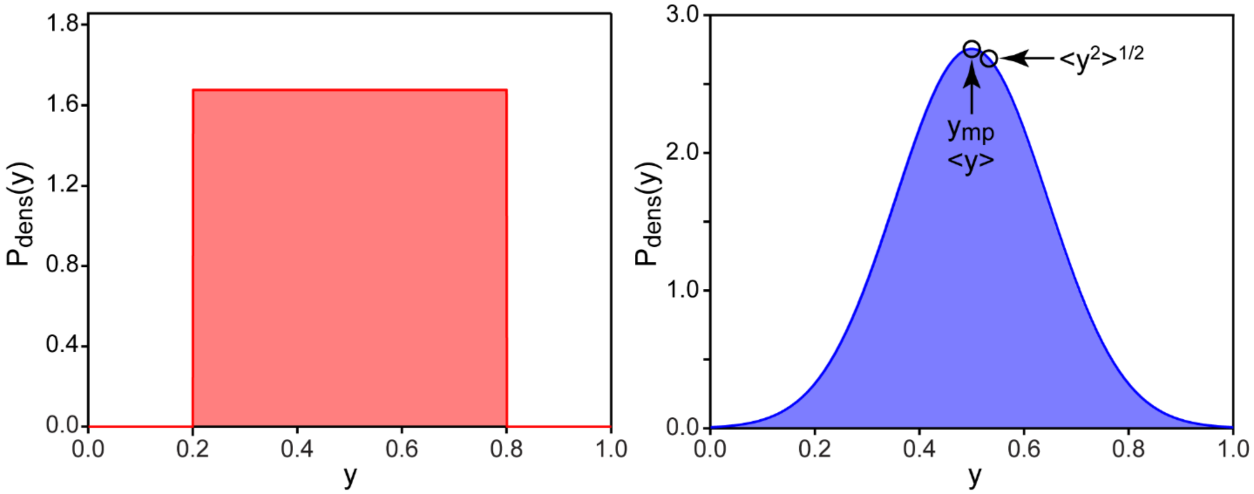


Figure 10.2. Two examples of common probability densities. Left: tophat, which applies to coin tosses and dice rolling. Right: Bell-shaped or Gaussian. These apply to your grades in Physical Chemistry. Shown are the coincident average and most probable values, and the root-mean-square average which is found at just a slighly higher value.

$$< v_x >_+ = \int_{0\ \mathrm{m/s}}^{\infty\ \mathrm{m/s}} v_x \cdot P_{dens}(v_x) \cdot \partial v_x$$

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:

$$\frac{\partial P_{dens}(y_{mp})}{\partial y} = 0$$

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 $\sqrt{< y^2 >}$ is near the top but to a slightly higher than the average. In fact it is generally true that $\sqrt{< y^2 >}$ is greater than $< y >$.

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 $\mathrm{E_i}$ is: $\frac{\mathrm{E_i}}{\sum_\mathrm{i}\mathrm{E_i}}$. 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: $\frac{e^{-E_i}}{\sum_i e^{-E_i}}$. However, there is one last problem which is that the argument of an exponential cannot have units. The answer is to divide $\mathrm{E_i}$ by $\mathrm{k_B T}$, which gives us the proper expression for Boltzmann's formula:

$$\mathrm{P_{dens}(E_i)} = \frac{\mathrm{e}^{-\mathrm{E_i}/\mathrm{k_B T}}}{\sum_\mathrm{i} \mathrm{e}^{-\mathrm{E_i}/\mathrm{k_B T}}}$$

Recall that the Boltzmann constant $\mathrm{k_B}$ is simply the S.I. gas constant R = 8.314 J/K/mol divided by Avogadro's number: $\mathrm{k_B} = \frac{\mathrm{R}}{\mathrm{N_A}} = 1.38 \times 10^{-23}$ 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. $\mathrm{E_i} = \frac{1}{2}\mathrm{mv}^2$. Therefore:

$$\mathrm{P_{dens}(v)} = \frac{\mathrm{e}^{\frac{-\mathrm{m}\cdot\mathrm{v}^2}{2\cdot\mathrm{k_B}\cdot\mathrm{T}}}}{\sum \mathrm{e}^{\frac{-\mathrm{m}\cdot\mathrm{v}^2}{2\cdot\mathrm{k_B}\cdot\mathrm{T}}}}$$

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 $\mathrm{v}^2 = \mathrm{v_x^2} + \mathrm{v_y^2} + \mathrm{v_z^2}$. The identity $\mathrm{e^{a+b+c}} = \mathrm{e^a} \cdot \mathrm{e^b} \cdot \mathrm{e^c}$ helps us show that:

$$\sum \mathrm{e}^{\frac{-\mathrm{m}\cdot\mathrm{v}^2}{2\cdot\mathrm{k_B}\cdot\mathrm{T}}} = \sum_{\mathrm{v_{x=-\infty}}}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot\mathrm{v_x^2}}{2\cdot\mathrm{k_B}\cdot\mathrm{T}}} \cdot \sum_{\mathrm{v_{y=-\infty}}}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot\mathrm{v_y^2}}{2\cdot\mathrm{k_B}\cdot\mathrm{T}}} \cdot \sum_{\mathrm{v_{z=-\infty}}}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot\mathrm{v_z^2}}{2\cdot\mathrm{k_B}\cdot\mathrm{T}}}$$

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: $\mathrm{v} = \sqrt{\mathrm{v_x^2 + v_y^2 + v_z^2}}$, 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: $\lim\limits_{n\to\infty} \sum_1^n \mathrm{f(x)} \cdot \left(\frac{\mathrm{b-a}}{\mathrm{n}}\right) = \int_{\mathrm{a}}^{\mathrm{b}} \mathrm{f(x)} \cdot \partial\mathrm{x}$. Based on this identity it's important that we have a factor like $\left(\frac{\mathrm{b-a}}{\mathrm{n}}\right)$ in our sum, which is the origin for ∂x for the integral.

When we examine a denominator term such as: $\sum_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_x^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}}$, it appears there is no such factor. And as usual, there is a clever answer, which is to multiply and divide the denominator by $\partial\mathrm{v_x}$ (and $\partial\mathrm{v_y}$ and $\partial\mathrm{v_z}$) which then allows us to transform the triple sum into a triple integral (bold for emphasis):

$$\frac{\mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v}^2}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}}}{\sum_{\mathrm{v_x}=-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_x^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \sum_{\mathrm{v_y}=-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_y^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \sum_{\mathrm{v_z}=-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_z^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}}} = \frac{\mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v}^2}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \boldsymbol{\partial}\mathbf{v_x} \cdot \boldsymbol{\partial}\mathbf{v_y} \cdot \boldsymbol{\partial}\mathbf{v_z}}{\int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_x^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \boldsymbol{\partial}\mathbf{v_x} \cdot \int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_y^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \boldsymbol{\partial}\mathbf{v_y} \cdot \int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_z^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \boldsymbol{\partial}\mathbf{v_z}}$$

First we will solve the denominator:

$$\left(\int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_x^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \partial\mathrm{v_x}\right) \cdot \left(\int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_y^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \partial\mathrm{v_y}\right) \cdot \left(\int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_z^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \partial\mathrm{v_z}\right)$$

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 $\int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_x^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \partial\mathrm{v_x}$ and then cube the result. We can look up a standard Gaussian-type integral:

$$\int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{a}\cdot \mathrm{x}^2} \cdot \partial\mathrm{x} = \left(\frac{\pi}{\mathrm{a}}\right)^{1/2}$$

To apply it to our expression we see: $\mathrm{a} = \frac{\mathrm{m}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}$, which makes the solution to the $\mathrm{v_x}$ integral:

$$\int_{-\infty}^{\infty} \mathrm{e}^{\frac{-\mathrm{m}\cdot \mathrm{v_x^2}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}} \cdot \partial\mathrm{v_x} = \left(\frac{\pi}{\frac{\mathrm{m}}{2\cdot \mathrm{k_B}\cdot \mathrm{T}}}\right)^{1/2} = \left(\frac{2\pi \cdot \mathrm{k_B}\cdot \mathrm{T}}{\mathrm{m}}\right)^{1/2}$$

And the triple integral can be evaluated:

$$\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_x^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_y^2}{2\cdot k_B\cdot T}}\cdot\partial v_y\right)\cdot\left(\int_{-\infty}^{\infty} e^{\frac{-m\cdot v_z^2}{2\cdot k_B\cdot T}}\cdot\partial v_z\right)=\left(\frac{2\pi\cdot k_B\cdot T}{m}\right)^{3/2}$$

This leaves the Boltzmann probability density in the form:

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v_x\cdot\partial v_y\cdot\partial v_z$$

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 ($\partial v$). 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

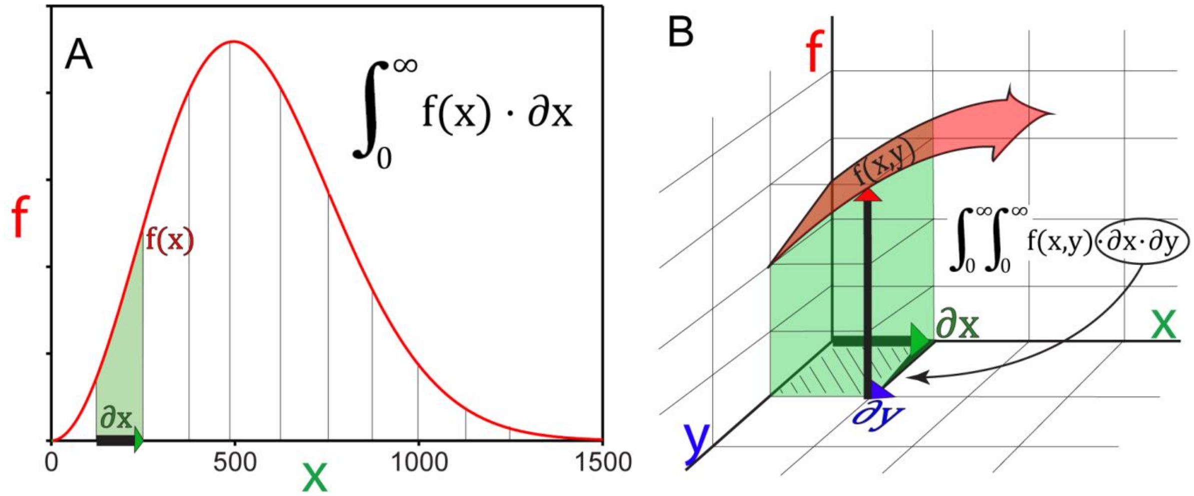


Figure 10.3. A. A partial has the effect of creating area (green shade) in a graph. The integral is the sum of these areas. **B.** A double partial creates volume elements, which are also summed in a 2-dimensional integral.

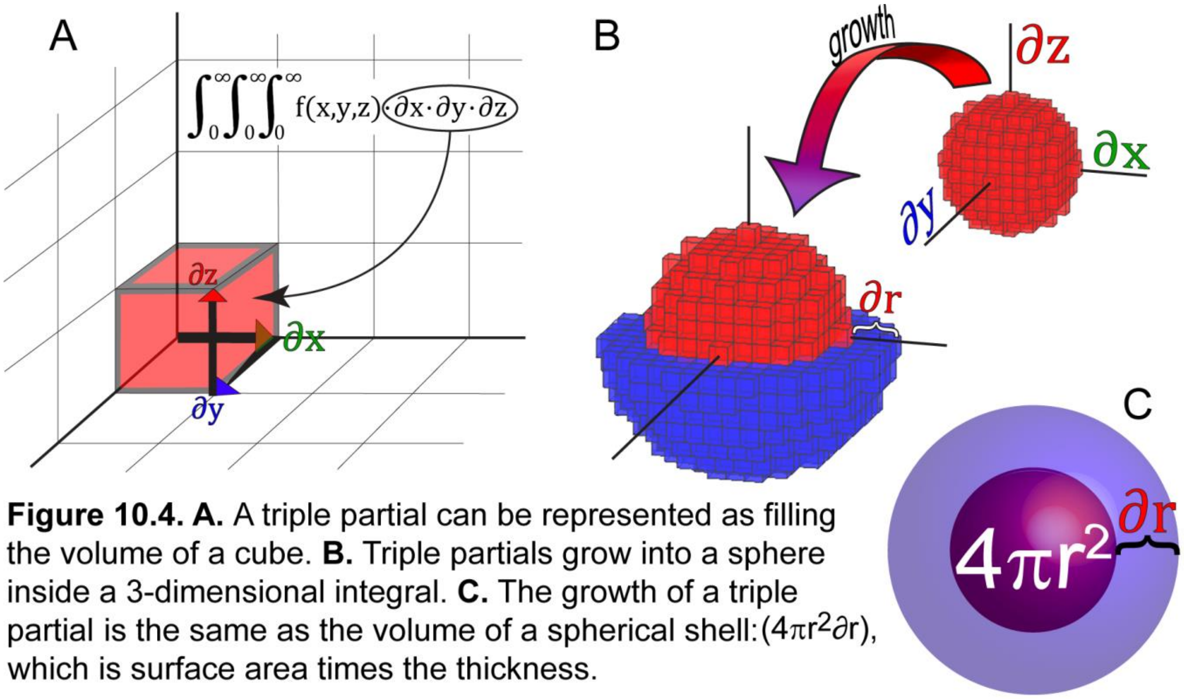


Figure 10.4. A. A triple partial can be represented as filling the volume of a cube. **B.** Triple partials grow into a sphere inside a 3-dimensional integral. **C.** The growth of a triple partial is the same as the volume of a spherical shell: $(4\pi r^2 \partial r)$, which is surface area times the thickness.

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:

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot \partial v_x\cdot \partial v_y\cdot \partial v_z$$

we now have the Maxwell-Boltzmann equation:

$$4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot \partial v$$

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.

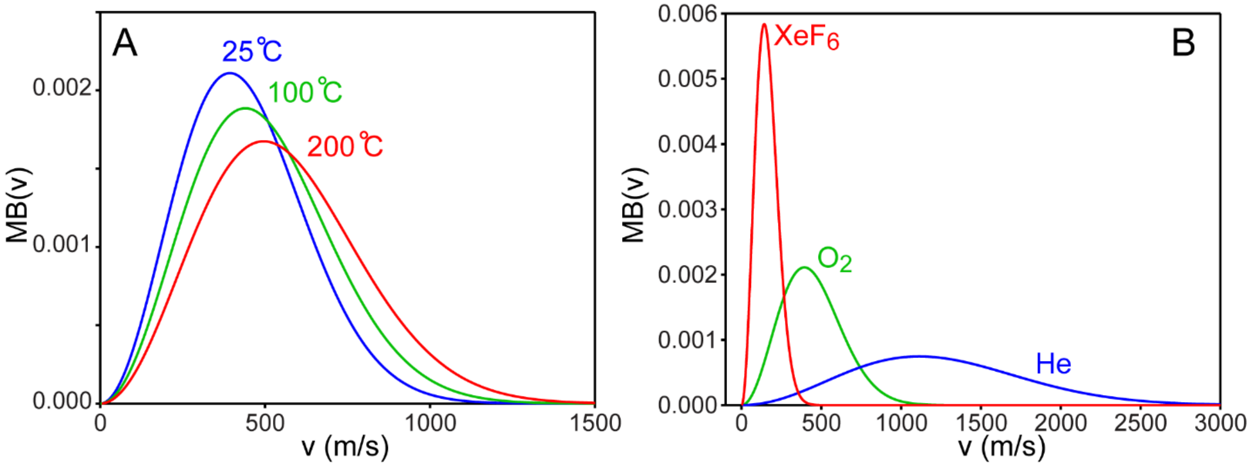


Figure 10.5. A. Maxwell-Boltzmann Distribution of O_2 gas at various temperatures. **B.** Different gases have substantially different distrubtions, with light materials such as helium experiencing extremely high velocities.

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:

$$\langle v \rangle = \int_0^\infty 4\pi \cdot v^2 \cdot v \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{3/2} \cdot e^{\frac{-m \cdot v^2}{2 \cdot k_B \cdot T}} \cdot \partial v$$

To simplify matters, we will call all the constants "Q" = $4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2}$, 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:

Integration by Parts

Integration by parts is necessary for solving some of the statistical problems we will be deriving in this chapter. The formula originates by first taking the derivative of the product of two functions f and g using the product rule:

$$\frac{\partial(f(x) \cdot g(x))}{\partial x} = \frac{\partial f(x)}{\partial x} \cdot g(x) + f(x) \cdot \frac{\partial g(x)}{\partial x}$$

Next we integrate it:

$$\int \frac{\partial(f(x) \cdot g(x))}{\partial x} \cdot \partial x = f(x) \cdot g(x) = \int \frac{\partial f(x)}{\partial x} \cdot g(x) \cdot \partial x + \int f(x) \cdot \frac{\partial g(x)}{\partial x} \cdot \partial x$$

After some rearrangement we get the familiar formula:

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

which is the integration by parts formula.

$$Q \cdot f(v) \cdot g(v)]_0^{\infty} = Q \cdot v^2 \cdot \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\bigg|_0^{\infty} = 0$$

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:

$$2 \cdot Q \cdot \frac{k_B \cdot T}{m} \int_0^{\infty} v \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v = 2 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right) \cdot \left(\frac{-k_B \cdot T}{m}\right) \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\bigg|_0^{\infty}$$

$$= -2 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right)^2 \cdot (e^{-\infty} - e^0) = 2 \cdot Q \cdot \left(\frac{k_B \cdot T}{m}\right)^2$$

Work through the constants (Q is defined above) to simplify them and you see:

$$\langle v \rangle = \int_0^{\infty} v \cdot 4 \cdot \pi \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{3/2} \cdot v^2 \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v = \left(\frac{8 \cdot k_B \cdot T}{\pi \cdot m}\right)^{1/2}$$

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:

$$\langle v^2 \rangle = \int_0^{\infty} 4\pi \cdot v^2 \cdot v^2 \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{3/2} \cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}} \cdot \partial v$$

Again we will remove all the constants by calling them $Q = 4 \cdot \pi \cdot \left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}$ 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:

$$\mathrm{Q} \cdot \mathrm{f(v)} \cdot \mathrm{g(v)} = \mathrm{Q} \cdot \mathrm{v}^3 \cdot \left(\frac{-\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right) \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}}\Bigg|_0^\infty = 0$$

since $\infty^3 \mathrm{e}^{-\infty} \rightarrow 0$ and $0^3 \mathrm{e}^{-0} \rightarrow 0$. The second term is:

$$-\mathrm{Q} \cdot \int_0^\infty \frac{\partial \mathrm{f(v)}}{\partial \mathrm{v}} \cdot \mathrm{g(v)} \cdot \partial \mathrm{v} = -\mathrm{Q} \cdot \int_0^\infty 3 \cdot \mathrm{v}^2 \cdot \left(\frac{-\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right) \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}} \cdot \partial \mathrm{v} =$$

$$\mathrm{Q} \cdot \int_0^\infty 3 \cdot \mathrm{v}^2 \cdot \left(\frac{\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right) \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}} \cdot \partial \mathrm{v}$$

which means we must do another integration by parts. We will define g(v) and $\frac{\partial \mathrm{g(v)}}{\partial \mathrm{v}}$ as above and now: $\mathrm{f(v)} = \mathrm{v}$ and $\frac{\partial \mathrm{f(v)}}{\partial \mathrm{v}} = 1$. Next, we factor out the constants:

$$3 \cdot \mathrm{Q} \cdot \frac{\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}} \cdot \int_0^\infty \mathrm{v} \cdot \mathrm{v} \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}} \cdot \partial \mathrm{v}$$

$$= 3 \cdot \mathrm{Q} \cdot \left(\frac{\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right) \cdot \mathrm{v} \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}}\Bigg|_0^\infty - 3 \cdot \mathrm{Q} \cdot \frac{\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}} \cdot \int_0^\infty \left(\frac{-\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right) \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}} \cdot \partial \mathrm{v}$$

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: $\int_0^\infty \mathrm{e}^{-\mathrm{a} \cdot \mathrm{v}^2} \cdot \partial \mathrm{v} = \frac{1}{2}\sqrt{\frac{\pi}{\mathrm{a}}}$. This allows us to demonstrate:

$$\langle \mathrm{v}^2 \rangle = \int_0^\infty \mathrm{v}^2 \cdot 4 \cdot \pi \cdot \left(\frac{\mathrm{m}}{2 \cdot \pi \cdot \mathrm{k_B} \cdot \mathrm{T}}\right)^{3/2} \cdot \mathrm{v}^2 \cdot \mathrm{e}^{\frac{-\mathrm{m} \cdot \mathrm{v}^2}{2 \cdot \mathrm{k_B} \cdot \mathrm{T}}} \cdot \partial \mathrm{v}$$

$$= 3 \cdot \mathrm{Q} \cdot \left(\frac{\mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right)^2 \cdot \frac{1}{2} \cdot \left(\frac{2 \cdot \pi \cdot \mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}\right)^{1/2}$$

Work through it (remember Q is defined above) and you find:

$$\langle \mathrm{v}^2 \rangle = \frac{3 \cdot \mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}$$

Often we express the above as the root-mean-squre, or rms velocity $\sqrt{\langle \mathrm{v}^2 \rangle} = \sqrt{\frac{3 \cdot \mathrm{k_B} \cdot \mathrm{T}}{\mathrm{m}}}$. 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

Gaussian Integral Identities

We hope that you could follow along the derivations on average velocities using integration by parts. However, we also live in the internet age, and it is effortless to find integral identities such as: $\int_0^\infty e^{-a\cdot x^2}\cdot\partial x=\frac{1}{2}\sqrt{\frac{\pi}{a}}$, $\int_0^\infty x^3\cdot e^{-a\cdot x^2}\cdot\partial x=\frac{1}{2a^2}$, and $\int_0^\infty x^4\cdot e^{-a\cdot x^2}\cdot\partial x=\frac{3\cdot\pi^{1/2}}{8a^{5/2}}$.

When applied to average velocity:

$$\langle v\rangle = Q\cdot\int_0^\infty v^3\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

We see that $a=\frac{m}{2\cdot k_B\cdot T}$ and thus $\langle v\rangle = Q\cdot\frac{4k_B{}^2\cdot T^2}{2m^2}=\left(\frac{8\cdot k_B\cdot T}{\pi\cdot m}\right)^{1/2}$. The same applies to average velocity squared:

$$\langle v^2\rangle = Q\cdot\int_0^\infty v^4\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\,\partial v$$

from which we find $\langle v^2\rangle = Q\cdot\frac{3\cdot\pi^{1/2}\cdot k_B{}^{5/2}\cdot T^{5/2}}{8m^{5/2}}=\frac{3\cdot k_B\cdot T}{m}$.

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:

$$\langle v^2\rangle = \frac{3\cdot k_B\cdot T}{m}\cdot\frac{N_A}{N_A}=\frac{3\cdot R\cdot T}{M}$$

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: $\partial\left(4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\right)/\partial v=$

$$8\pi\cdot v\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}+4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot\left(\frac{-m\cdot v}{k_B\cdot T}\right)\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}$$

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:

$$8\pi \cdot v_{mp} \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{3/2} \cdot e^{\frac{-m \cdot v_{mp}^2}{2 \cdot k_B \cdot T}} = 4\pi \cdot v_{mp}^2 \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{3/2} \cdot \left(\frac{m \cdot v_{mp}}{k_B \cdot T}\right) \cdot e^{\frac{-m \cdot v_{mp}^2}{2 \cdot k_B \cdot T}}$$

Several simplifications can me made: $2 = v_{mp} \cdot \left(\frac{m \cdot v_{mp}}{k_B \cdot T}\right)$ from which we solve:

$$v_{mp} = \sqrt{\frac{2 \cdot k_B \cdot T}{m}}$$

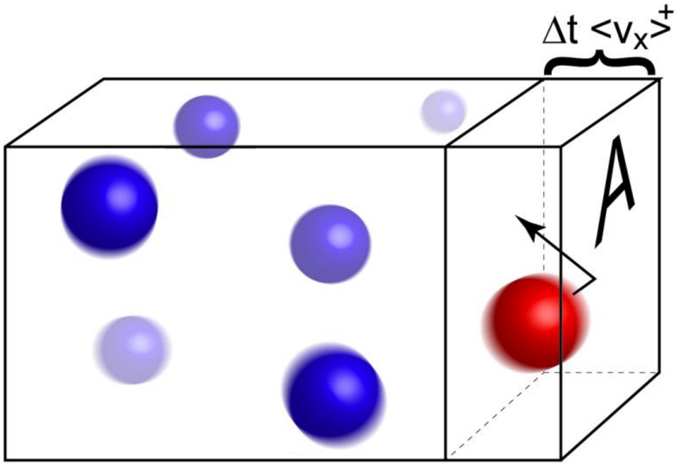


Figure 10.6. The flux of gas molecules hitting an area is calculated using the average positive directional velocity.

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:$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{1/2} \cdot e^{\frac{-m \cdot v_x^2}{2 \cdot k_B \cdot T}} \cdot \partial v_x$, 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:

$$\langle v_x \rangle^+ = \int_0^{\infty} v_x \cdot \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{1/2} \cdot e^{\frac{-m \cdot v_x^2}{2 \cdot k_B \cdot T}} \cdot \partial v_x$$

(see the change in the lower limit?) This is solved with the identity $\int_0^{\infty} x \cdot e^{-a \cdot x^2} \cdot \partial x = \frac{1}{2a}$:

$$\langle v_x \rangle^+ = \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{1/2} \cdot \frac{1}{2a} = \left(\frac{m}{2 \cdot \pi \cdot k_B \cdot T}\right)^{1/2} \cdot \frac{2 \cdot k_B \cdot T}{2m} = \left(\frac{k_B \cdot T}{2\pi \cdot m}\right)^{1/2}$$

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:

$$\#collisions = A \cdot \Delta t \cdot \langle v_x \rangle^+ \cdot \frac{N}{V} = A \cdot \Delta t \cdot \left(\frac{k_B \cdot T}{2\pi \cdot m}\right)^{1/2} \cdot \frac{N}{V}$$

Last, recall that the flux is the number of collisions per unit area per unit time. Consequently:

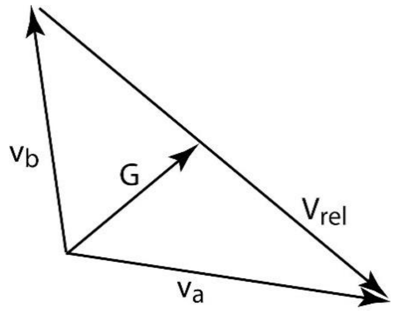
$$Flux = \frac{A \cdot \Delta t \cdot \left(\frac{k_B \cdot T}{2\pi \cdot m}\right)^{1/2} \cdot \frac{N}{V}}{A \cdot \Delta t} = \left(\frac{k_B \cdot T}{2\pi \cdot m}\right)^{1/2} \cdot \frac{N}{V}$$

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: $\frac{P}{k_B \cdot T} = \frac{N}{V}$. When we use this in the expression above we determine that:

$$Flux = \left(\frac{k_B \cdot T}{2\pi \cdot m}\right)^{1/2} \cdot \frac{P}{k_B \cdot T} = \frac{P}{\sqrt{2\pi \cdot m \cdot k_B \cdot T}}$$

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:

$$MB(v_a) \cdot MB(v_b) = \left(\frac{1}{2\pi k_B T}\right)^3 \cdot (m_a m_b)^{3/2} \cdot e^{-\frac{m_b {v_b}^2 + m_a {v_a}^2}{2k_B T}}$$

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: $\left(\frac{1}{2\pi k_B T}\right)^{3/2}$ 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: $\mathrm{m_b v_a^2 + m_a v_a^2}$ that appears in the exponential in terms of V$_{\mathrm{rel}}$ and G. We expressed $\mathrm{v_a}$ and $\mathrm{v_b}$ above, and now we square them and do some algebra. There is a cross term **G·V$_{\mathrm{rel}}$** that has been made bold for emphasis:

$$\mathrm{m_b v_b^2 + m_a v_a^2}$$

$$= \mathrm{m_b}\left[\mathrm{G^2} + \frac{\mathrm{m_a^2}}{(\mathrm{m_a}+\mathrm{m_b})^2}\mathrm{V_{rel}^2} - \frac{\mathbf{2m_a}}{\mathbf{m_a}+\mathbf{m_b}}\mathbf{G}\cdot\mathbf{V_{rel}}\right] + \mathrm{m_a}\left[\mathrm{G^2} + \frac{\mathrm{m_b^2}}{(\mathrm{m_a}+\mathrm{m_b})^2}\mathrm{V_{rel}^2} + \frac{\mathbf{2m_b}}{\mathbf{m_a}+\mathbf{m_b}}\mathbf{G}\cdot\mathbf{V_{rel}}\right]$$

$$= (\mathrm{m_a}+\mathrm{m_b})\mathrm{G^2} + \left[\frac{\mathrm{m_b}\cdot\mathrm{m_a^2} + \mathrm{m_a}\cdot\mathrm{m_b^2}}{(\mathrm{m_a}+\mathrm{m_b})^2}\right]\mathrm{V_{rel}^2}$$

$$= (\mathrm{m_a}+\mathrm{m_b})\mathrm{G^2} + \frac{\mathrm{m_a}\cdot\mathrm{m_b}}{(\mathrm{m_a}+\mathrm{m_b})}\mathrm{V_{rel}^2}$$

Notice how above that the **G·V$_{\mathrm{rel}}$** cross terms in the second step cancel? This simplifies the remaining derivation because we can now separate the G and V$_{\mathrm{rel}}$. as shown here:

$$\mathrm{MB(G)\cdot MB(V_{rel})} = \left(\frac{(\mathrm{m_a m_b})^{1/2}}{2\pi \mathrm{k_B T}}\right)^3 \cdot e^{-\frac{(\mathrm{m_a}+\mathrm{m_b})\mathrm{G^2}}{2\mathrm{k_B T}}} \cdot e^{-\frac{\frac{\mathrm{m_a m_b}}{\mathrm{m_a}+\mathrm{m_b}}\mathrm{V_{rel}^2}}{2\mathrm{k_B T}}}$$

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 $\mathrm{MB(v_a)\cdot MB(v_b)}$, of course it uses partials of $\partial\mathrm{v_a}\cdot\partial\mathrm{v_b}$. When transforming: $\partial\mathrm{v_a}\cdot\partial\mathrm{v_b} \rightarrow \partial\mathrm{G}\cdot\partial\mathrm{V_{rel}}$, the geometry factor (also known as the "Jacobian") is 1.0; see the Appendix. This means:

$$\mathrm{MB(v_a)\cdot MB(v_b)\cdot \partial v_a \cdot \partial v_b = MB(G)\cdot MB(V_{rel})\cdot \partial G\cdot \partial V_{rel}}$$

However, we still need to remember that we live in three dimensions. Consequently the expression is:

$$\left(\frac{(\mathrm{m_a m_b})^{1/2}}{2\pi \mathrm{k_B T}}\right)^3 e^{-\frac{(\mathrm{m_a}+\mathrm{m_b})(\mathrm{G_x}^2+\mathrm{G_y}^2+\mathrm{G_z}^2)}{2\mathrm{k_B T}}} e^{-\frac{\frac{\mathrm{m_a m_b}}{\mathrm{m_a}+\mathrm{m_b}}\mathrm{V_{rel}^2}}{2\mathrm{k_B T}}} \partial\mathrm{V_{rel,x}}\,\partial\mathrm{V_{rel,y}}\,\partial\mathrm{V_{rel,z}}\,\partial\mathrm{G_x}\,\partial\mathrm{G_y}\,\partial\mathrm{G_z}$$

Ultimately, we want $\langle\mathrm{V_{rel}}\rangle$, so we want to remove all the reduced mass velocities (the G's). To do so we integrate them out from $-\infty<\mathrm{G_{x,y,z}}<\infty$:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(\frac{(\mathrm{m_a m_b})^{1/2}}{2\pi \mathrm{k_B T}}\right)^3 e^{-\frac{(\mathrm{m_a}+\mathrm{m_b})(\mathrm{G_x}^2+\mathrm{G_y}^2+\mathrm{G_z}^2)}{2\mathrm{k_B T}}}\partial\mathrm{G_x}\,\partial\mathrm{G_y}\,\partial\mathrm{G_z} = \left(\frac{(\mathrm{m_a m_b})}{2\pi\mathrm{k_B T}(\mathrm{m_a}+\mathrm{m_b})}\right)^{3/2}$$

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:

$$\left(\frac{(m_a m_b)}{2\pi k_B T(m_a + m_b)}\right)^{3/2} e^{-\frac{(m_a m_b)V_{rel}^2}{2k_B T(m_a+m_b)}} \cdot \partial V_{rel,x}\,\partial V_{rel,y}\,\partial V_{rel,z}$$

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 $\frac{(m_a m_b)}{(m_a+m_b)}$. We can work the average relative velocity expression:

$$\langle V_{rel}\rangle = \int_0^\infty 4\pi \cdot {V_{rel}}^3 \cdot \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \cdot e^{-\frac{\mu \cdot {V_{rel}}^2}{2k_B T}} \cdot \partial V_{rel} = \left(\frac{8 \cdot k_B \cdot T}{\pi \cdot \mu}\right)^{\frac{1}{2}}$$

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 √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

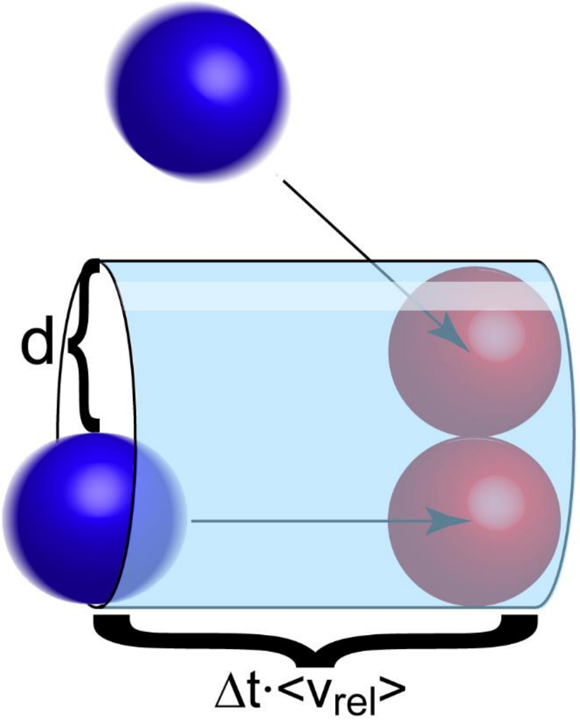


Figure 10.8. Collision volume is defined by the relative velocities of two gas molecules and the diameter.

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: $\frac{N}{V} = \frac{P}{k_B \cdot T}$ 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 5.8×10^9 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.

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:

$$\partial \mathrm{v}_{\mathrm{x}} \cdot \partial \mathrm{v}_{\mathrm{y}} \cdot \partial \mathrm{v}_{\mathrm{z}} = \left|\frac{\partial(\mathrm{v}_{\mathrm{x}}, \mathrm{v}_{\mathrm{y}}, \mathrm{v}_{\mathrm{z}})}{\partial(\mathrm{v}, \theta, \phi)}\right| \cdot \partial \mathrm{v} \cdot \partial \phi \cdot \partial \theta = \mathrm{v}^2 \cdot \sin(\phi) \cdot \partial \mathrm{v} \cdot \partial \phi \cdot \partial \theta$$

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:

$$\mathrm{v}_{\mathrm{x}} = \mathrm{v} \cdot \sin(\phi) \cdot \cos(\theta)$$

$$\mathrm{v}_{\mathrm{y}} = \mathrm{v} \cdot \sin(\phi) \cdot \sin(\theta)$$

$$\mathrm{v}_{\mathrm{z}} = \mathrm{v} \cdot \cos(\phi)$$

where $\mathrm{v} = \sqrt{\mathrm{v}_{\mathrm{x}}^2 + \mathrm{v}_{\mathrm{y}}^2 + \mathrm{v}_{\mathrm{z}}^2}$. The Jacobian $\left|\frac{\partial(\mathrm{v}_{\mathrm{x}}, \mathrm{v}_{\mathrm{y}}, \mathrm{v}_{\mathrm{z}})}{\partial(\mathrm{v}, \theta, \phi)}\right|$ is the absolute values of the determinant of the following matrix:

$$\left|\det\begin{bmatrix} \frac{\partial \mathrm{v}_{\mathrm{x}}}{\partial \mathrm{v}} & \frac{\partial \mathrm{v}_{\mathrm{x}}}{\partial \theta} & \frac{\partial \mathrm{v}_{\mathrm{x}}}{\partial \varphi} \\ \frac{\partial \mathrm{v}_{\mathrm{y}}}{\partial \mathrm{v}} & \frac{\partial \mathrm{v}_{\mathrm{y}}}{\partial \theta} & \frac{\partial \mathrm{v}_{\mathrm{y}}}{\partial \varphi} \\ \frac{\partial \mathrm{v}_{\mathrm{z}}}{\partial \mathrm{v}} & \frac{\partial \mathrm{v}_{\mathrm{z}}}{\partial \theta} & \frac{\partial \mathrm{v}_{\mathrm{z}}}{\partial \varphi} \end{bmatrix}\right|$$

In our coordinate system the absolute value of the determinant of the matrix is:

$$\left|\det\begin{bmatrix} \sin(\phi)\cos(\theta) & -\mathrm{v}\sin(\phi)\sin(\theta) & \mathrm{v}\cos(\phi)\cos(\theta) \\ \sin(\phi)\sin(\theta) & \mathrm{v}\sin(\phi)\cos(\theta) & \mathrm{v}\cos(\phi)\sin(\theta) \\ \cos(\phi) & 0 & -\mathrm{v}\sin(\phi) \end{bmatrix}\right|$$

$$\begin{aligned} &= |-\mathrm{v}^2\sin^3(\phi)\cos^2(\theta) - \mathrm{v}^2\sin(\phi)\cos^2(\phi)\sin^2(\theta) + 0 - \mathrm{v}^2\sin^3(\phi)\sin^2(\theta) - 0 \\ &\qquad - \mathrm{v}^2\sin(\phi)\cos^2(\phi)\cos^2(\theta)| \\ &= |-\mathrm{v}^2\sin^3(\phi)(\cos^2(\theta) + \sin^2(\theta)) - \mathrm{v}^2\sin(\phi)\cos^2(\phi)(\sin^2(\theta) + \cos^2(\theta))| \\ &= |-\mathrm{v}^2\sin^3(\phi) - \mathrm{v}^2\sin(\phi)\cos^2(\phi)| \\ &= |-\mathrm{v}^2\sin(\phi)(\sin^2(\phi) + \cos^2(\phi))| \\ &= |-\mathrm{v}^2\sin(\phi)| \end{aligned}$$

Since we take the absolute value of this result (the negative sign goes away), the final answer is:

$$\partial \mathrm{v}_{\mathrm{x}} \cdot \partial \mathrm{v}_{\mathrm{y}} \cdot \partial \mathrm{v}_{\mathrm{z}} = \mathrm{v}^2 \cdot \sin(\phi) \cdot \partial \mathrm{v} \cdot \partial \phi \cdot \partial \theta$$

When we apply the Jacobian to the Maxwell-Boltzmann formula we see that (bold emphasis added):

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot \boldsymbol{\partial v_x\cdot\partial v_y\cdot\partial v_z} = \left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot \boldsymbol{v^2\cdot\sin(\phi)\cdot\partial v\cdot\partial\phi\cdot\partial\theta}$$

Now we can integrate out the angles:

$$\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot v^2\cdot\sin(\phi)\cdot\partial v\cdot\int_0^{2\pi}\sin(\phi)\cdot\partial\phi\cdot\int_0^{\pi}\partial\theta$$

which leaves us with just a constant:

$$\int_0^{\pi}\sin(\phi)\cdot\partial\phi\cdot\int_0^{2\pi}\partial\theta = -\cos(\phi)]_0^{\pi}\cdot 2\pi = 4\pi$$

leaving us with:

$$4\pi\cdot v^2\cdot\left(\frac{m}{2\cdot\pi\cdot k_B\cdot T}\right)^{3/2}\cdot e^{\frac{-m\cdot v^2}{2\cdot k_B\cdot T}}\cdot\partial v$$

This is the velocity form of the Maxwell-Boltzmann equation.

A.2. $\boldsymbol{\partial v_a\cdot\partial v_b\to\partial G\cdot\partial V_{rel}}$: 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:

$$\left|\frac{\partial(v_a, v_b)}{\partial(G, V_{rel})}\right| = \left|\det\begin{bmatrix}\frac{\partial v_a}{\partial V_{rel}} & \frac{\partial v_a}{\partial G}\\ \frac{\partial v_b}{\partial V_{rel}} & \frac{\partial v_b}{\partial G}\end{bmatrix}\right|$$

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:

$$\left|\det\begin{bmatrix}\frac{m_b}{m_a+m_b} & 1\\ -\frac{m_a}{m_a+m_b} & 1\end{bmatrix}\right| = \frac{m_b}{m_a+m_b}+\frac{m_a}{m_a+m_b} = \frac{m_a+m_b}{m_a+m_b} = 1$$

Done!

Problems: Numerical

1. Some of you asked why is the r.m.s. average of something greater than the average of something (the “something” can be the velocities of gas molecules for example). The reason is because there is a distribution in the velocities, i.e. some gases are moving fast, and some are slow. To demonstrate:

a. Take the last 5 digits of your University ID number as a set of digits; mine is: {9, 8, 5, 3, 9}. Calculate the average value of this set. **(2 pts)**

b. Now square each of the give numbers in your set, and calculate the average of the squared numbers. Take the square root of that; this is the r.m.s. average. Which is higher? **(2 pts)**

c. Now repeat parts a & b with a set of five numbers that are your favorite number (for me its 8). Now what is the relationship between the average and r.m.s. average? **(2 pts)**

2. Let us say you have two probability densities, and you must solve their normalizers:

a. Probability density for number of cats: $\frac{e^{-2\cdot \mathrm{cat}}}{\sum_{\mathrm{number\_cats}} e^{-2\cdot \mathrm{cat}}}$, and:

b. Probability density for water volume: $\frac{e^{-\mathrm{water}/2}}{\sum_{\mathrm{water\_volume}} e^{-\mathrm{water}/2}}$

There are limits of 0 (lower) and ∞ (upper) for both the number of cats and for water volume.

Here are two identities: $\int_0^\infty e^{-a\cdot x}\,\partial x = \frac{1}{a}$ and: $\sum_{n=0}^{n=\infty} e^{-a\cdot n} = \frac{1}{1-e^{-a}}$ (requires $n = 0,1,2,3\ ...$)

Please evaluate the normalizer in each case using the identities above. **(5 pts each)**

Hint: The normalizer is the denominator. **Double Hint:** The denominator is the bottom part.

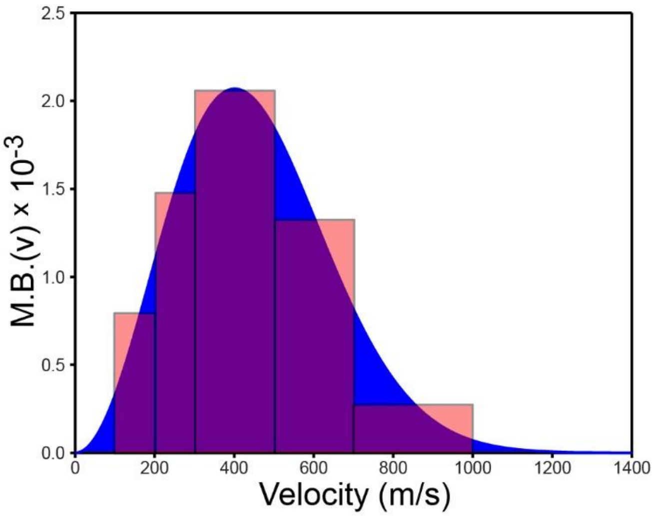
c. You should have used one identity for problem a. and the other for b. What guided your choice of identity? **(3 pts)**

3. Let us solve for the average number of cats per house using the probability distribution:

$$\mathrm{Probdist(cat)} = 0.8647 \cdot e^{-2\cdot \mathrm{cat}}$$

And determine ⟨cat⟩ considering homes with either 0, 1 or 2 kitties by filling out the following table. The sum of one of these columns is ⟨cat⟩ (please identify it). **(7 pts)**

# Cats	Probdist(cat)	Probdist(cat) · cat
0		
1		
2		
Sum:		



4. When it comes to evaluating integrals, there are two ways you can do it. First, you can use standard calculus. You should also know that the integration of a function is the area under a curve. The area can be approximated using the sum of the areas of a bunch of rectangles as shown in the figure on the right. For this problem, you will lean how Maxwell-Boltzmann integrals really work using the rectangles shown in the figure to determine the area under the Maxwell-Boltzmann distribution and the average velocity of oxygen gas at 310 K. To do so, fill out the following table:

Range (m/s)	Δv (m/s)	MB(v)	Area	Area × mid-velocity (m/s)
100-200	100	6. 8301×10^{-4}	0.0683	10.2452
200-300	100			
300-500	200			
500-700	200			
700-1000	300			

Here you see where we defined the rectangles in velocity (the length of the x-dimension) and you have to insert the result of the Maxwell-Boltzmann distribution function (the length in the y-direction). The area is the x-length times the y-length. The mid-velocity is defined as 150 m/s for the 100-200 m/s range, etc.

a. Fill out the remaining table. **(10 pts)**

b. What do the areas sum to? Why does this make sense? **(3 pts)**

c. What do the areas×velocities sum to? **(5 pts)**

5. Assume perfect gas behavior: If I am incubating a patient with 8.935 g O_2 at a slightly elevated pressure of 1.2 bars, what is the mean speed of the molecules? Note that an average lung size is 6 liters. **(5 pts)**

6. a. What fraction of molecules move slower their most probable speed $v_{mp}= \left(\frac{2 \cdot k_B \cdot T}{m}\right)^{1/2}$? **(10 pts)**

b. How many are moving faster? (pt. b. doesn't require integration of the Maxwell-Boltzmann distribution if you got pt a. right.) **(3 pts)**

Hint: Here is the standard definite integral you definitely need to use:

$$\int_0^c v^2 e^{-a \cdot v^2} \cdot \partial v = \left(\frac{\pi}{16a^3}\right)^{1/2} \cdot \operatorname{erf}\left(c \cdot a^{1/2}\right) - \left(\frac{c}{2a}\right) \cdot e^{-c^2 \cdot a}$$

The "erf" is called the error function. It's related to the area under a Gaussian curve and has the form of a very long Taylor series, which is why you usually just give it a number and it returns another number; the erf function should be a feature of your calculator or you can use google, i.e. search for: erf(1.0) and it will return 0.8427.

7. a. What fraction of molecules move slower than the RMS speed $v_{rms}= \left(\frac{3 \cdot k_B \cdot T}{m}\right)^{1/2}$? **(10 pts)**

b. How many are moving faster? (pt. b. doesn't require integration of the Maxwell-Boltzmann distribution if you got pt a. right.) **(3 pts)**

Hint: Here is the standard definite integral you definitely need to use:

$$\int_0^c v^2 e^{-av^2} dv = \left(\frac{\pi}{16a^3}\right)^{1/2} \cdot \mathrm{erf}\left(c \cdot a^{1/2}\right) - \frac{c}{2a} e^{-c^2 \cdot a}$$

The "erf" is called the error function. It's related to the area under a Gaussian curve and has the form of a very long Taylor series, which is why you usually just give it a number and it returns another number; the erf function should be a feature of your calculator or you can use google, i.e. search for: erf(1.2247) and it will return 0.9167.

8. Let's say I have Argon gas and I want to compress it so much that the mean free path is as big as the atom itself (0.34 nm diameter). At 25 °C, how much should I pressurize the gas?

The equation for mean free path (λ) is: $\lambda = \frac{k_B \cdot T}{\sqrt{2} \cdot \pi \cdot d^2 \cdot P}$ **(5 pts)**

9. Let's say I have water vapor gas at 100 °C and I want to compress it so much that the mean free path is as big as the molecule itself (0.27 nm diameter). How much should I pressurize the gas? The equation for mean free path (λ) is: $\lambda = \frac{k_B \cdot T}{\sqrt{2} \cdot \pi \cdot d^2 \cdot P}$ **(5 pts)**

Problems: Theoretical or Explain in Words

1. a. If I was to find the average value of **positive momentum** in the x-direction (p_x), what would be the proper limits of integration (upper and lower limits):

$$\int_?^? p_x \cdot \mathrm{Probdist}(p_x) \cdot \partial p_x = \int_{\mathrm{lower\_limit?}}^{\mathrm{upper\_limit?}} p_x \cdot \left(\frac{1}{2\pi \cdot m \cdot k_B T}\right)^{\frac{1}{2}} \cdot e^{\frac{-p^2}{2 \cdot m \cdot k_B T}} \cdot \partial p$$

What I mean by average positive momentum is that, if I were to average the momenta of a collection of gases, I wouldn't average in a molecule's data if it was going "backwards". **(3 pts)**

b. Evaluate the average positive momentum in the x dimension $\langle p_x \rangle$. **(7 pts)**

2. Here is the function for the net momentum of gas molecules:

$$4\pi \cdot p^2 \cdot \left(\frac{1}{2\pi \cdot m \cdot k_B T}\right)^{\frac{3}{2}} \cdot e^{\frac{-p^2}{2 \cdot m \cdot k_B T}}$$

Can you show that this probability distribution is normalized? Hint: the proper limits of integration are 0 to ∞.

(7 pts)

3. The Maxwell-Boltzmann Distribution as a function of momentum is:

$$MB(p) \cdot \partial p = 4\pi \cdot p^2 \cdot \left(\frac{1}{2\pi \cdot m \cdot k_B T}\right)^{\frac{3}{2}} \cdot e^{\frac{-p^2}{2 \cdot m \cdot k_B T}} \cdot \partial p$$

Let's rewrite the same as a function of energy which is $E = \frac{p^2}{2m}$. This is a very easy two-step process; first, wherever you see a "p" in the MB distribution, write it instead as a function of E. This means replacing each instance of p with $\sqrt{2mE}$. Almost done! There is one last part that is a small bit harder- you can't just replace ∂p with ∂E, but instead you have to change it as:

$$\left|\frac{\partial p(E)}{\partial E}\right| \cdot \partial E$$

As such, this very long-worded question is actually asking you to simplify: **(10 pts)**

$$4 \cdot \pi \cdot p(E)^2 \cdot \left(\frac{1}{2\pi \cdot m \cdot k_B T}\right)^{\frac{3}{2}} \cdot e^{\frac{-p(E)^2}{2 \cdot m \cdot k_B \cdot T}} \cdot \left|\frac{\partial p(E)}{\partial E}\right| \cdot \partial E$$

4. The Maxwell-Boltzmann distribution as function of energy is: **(10 pts)**

$$MB(E) = 2 \cdot \sqrt{\frac{E}{\pi}} \cdot \left(\frac{1}{k_B T}\right)^{\frac{3}{2}} \cdot e^{\frac{-E}{k_B T}}$$

Can you calculate the most probable energy (E_{mp}) of a gas phase molecule from the above?

5. The collision frequency for a gas (Z) was determined in class to be:

$$Z = \frac{P}{k_B T} \cdot \pi d^2 \cdot \langle v_{rel} \rangle = \frac{P}{k_B T} \cdot \pi d^2 \cdot \sqrt{\frac{8 k_B T}{\pi \mu}}$$

a. Now, the question is, if the gas is in a balloon and is heated up, does the collision frequency increase or decrease? Hint: the balloon would expand if heated to keep the pressure constant. **(4 pts)**

b. If instead the gas is in a metal container and heated up, does the collision frequency increase or decrease? **(4 pts)**

Hint: This isn't so much a trick question as it is a tricky question. Also $PV = nRT$.

Chapter 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, ν is the frequency of light, c is the speed of light and λ 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

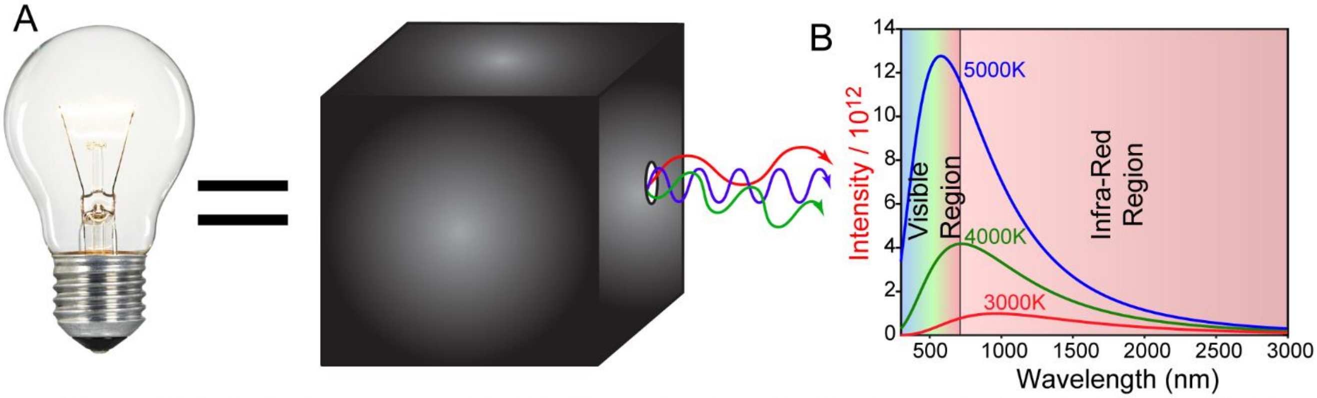


Figure 11.1. A. An incandescent light bulb can be described by the emission of a hot, completely self-absorptive black box. **B.** Emission specra of a black box radiator as a function of temperature. At ~5000K the emission is "white light" and bears many similarities with the solar spectrum.

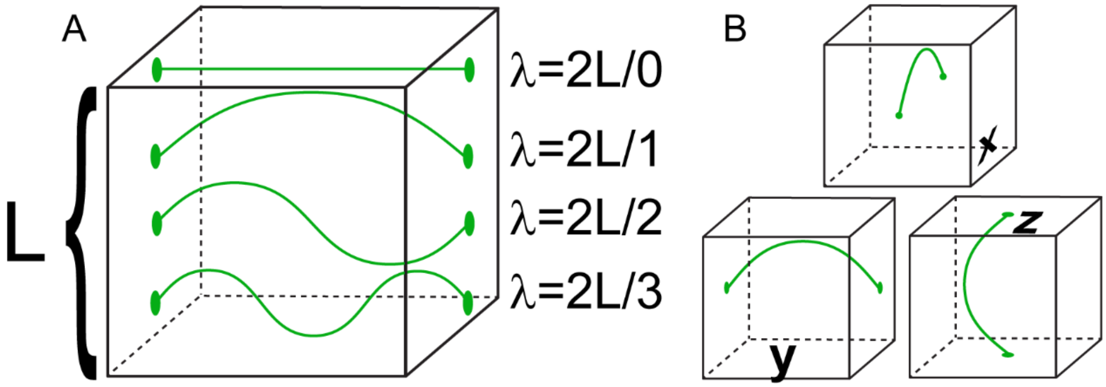


Figure 11.2. A. Light waves can fit in the black box over multiple wavelengths as a function of λ=2L/n (n=0,1,2,...), where n is the net mode number. **B.** There is a "mode" for every dimension.

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 λ=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 $\{n_x, n_y, n_z\}$ 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:

$$\mathrm{E(x, y, z)} = \sin\left(\frac{\mathrm{n_x}\pi}{\mathrm{L}} \cdot \mathrm{x}\right) \cdot \sin\left(\frac{\mathrm{n_y}\pi}{\mathrm{L}} \cdot \mathrm{y}\right) \cdot \sin\left(\frac{\mathrm{n_z}\pi}{\mathrm{L}} \cdot \mathrm{z}\right)$$

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.

$$\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z}\right\} \mathrm{E(x, y, z, t)} = \frac{-1}{c^2}\frac{\partial^2}{\partial t^2} \mathrm{E(x, y, z, t)}$$

When we insert our relationship we find:

$$\mathrm{E(y, z, t)}\frac{\partial^2}{\partial x^2}\sin\left(\frac{\mathrm{n_x}\pi}{\mathrm{L}} \cdot \mathrm{x}\right) + \mathrm{E(x, z, t)}\frac{\partial^2}{\partial y^2}\sin\left(\frac{\mathrm{n_y}\pi}{\mathrm{L}} \cdot \mathrm{y}\right) + \mathrm{E(x, y, t)}\frac{\partial^2}{\partial z}\sin\left(\frac{\mathrm{n_z}\pi}{\mathrm{L}} \cdot \mathrm{z}\right) = \mathrm{E(x, y, z)}\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\sin\left(\frac{2\pi \mathrm{c}}{\lambda} \cdot \mathrm{t}\right)$$

We can evaluate terms such as:

$$\mathrm{E(y, z, t)}\frac{\partial^2}{\partial \mathrm{x}^2}\sin\left(\frac{\mathrm{n_x}\pi}{\mathrm{L}} \cdot \mathrm{x}\right) = -\frac{\mathrm{n_x^2}\pi^2}{\mathrm{L}^2}\mathrm{E(x, y, z, t)}$$

Which makes:

$$\mathrm{E(x, y, z, t)}\left\{\frac{\mathrm{n_x^2}\pi^2}{\mathrm{L}^2} + \frac{\mathrm{n_y^2}\pi^2}{\mathrm{L}^2} + \frac{\mathrm{n_z^2}\pi^2}{\mathrm{L}^2}\right\} = \mathrm{E(x, y, z, t)}\frac{4\pi^2}{\lambda^2}$$

The equation for the electric field can be divided out on the left and right sides leaving:

$$\frac{\pi^2}{\mathrm{L}^2}\left(\mathrm{n_x^2} + \mathrm{n_y^2} + \mathrm{n_z^2}\right) = \frac{4\pi^2}{\lambda^2}$$

If we simply treat the mode set like a vector, which has a net value:

$$\mathrm{n}^2 = \mathrm{n_x^2} + \mathrm{n_y^2} + \mathrm{n_z^2}$$

then the above simplifies to:

$$\lambda^2 = \frac{4L^2}{n^2} \text{ or } \lambda = \frac{2L}{n}$$

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 $= 1$; they are $\{1,0,0\}, \{0,1,0\}$ and $\{0,0,1\}$. Likewise a mode number of $n = \sqrt{2}$ can also come about from three sets, $\{1,0,1\}, \{1,1,0\}$ 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
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.

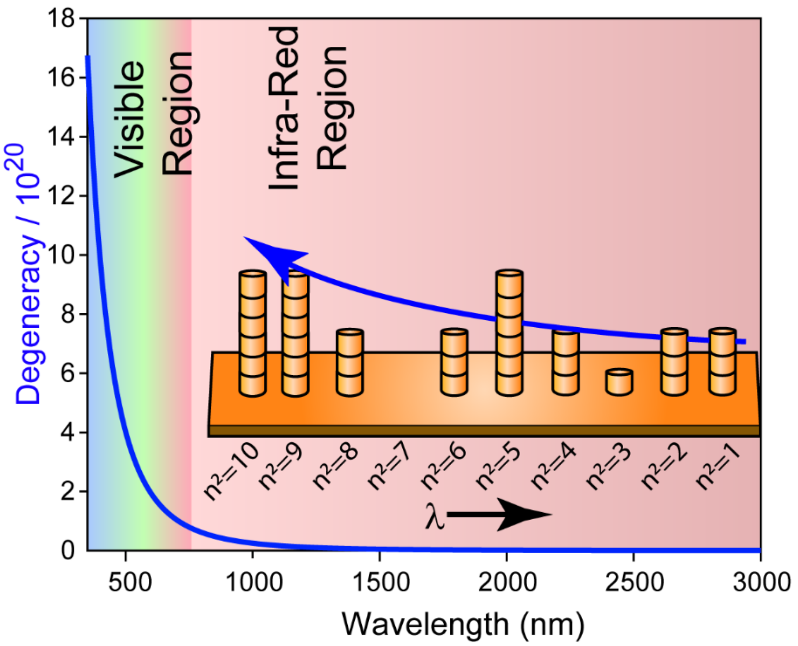


Figure 11.3. The box wavelengths can be viewed as posts that photons are stacked upon. The trend is upward as the net mode number "n" increases. The solid line is the analytical result for a $1\ cm^3$ box, and is proportional to λ^{-4}.

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

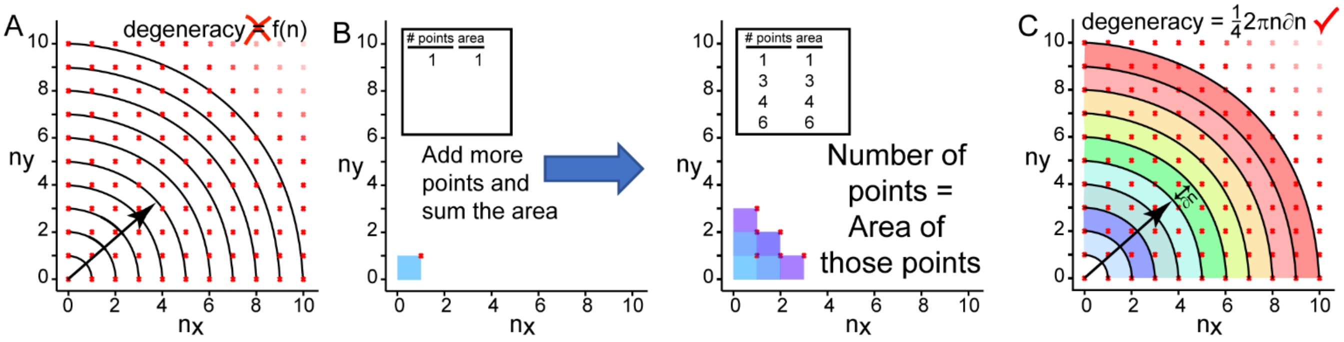


Figure 11.4 A. There is no simple relationship between the number of modes {nx, ny} and the corresponding net mode number n. **B.** Each unique set of mode numbers {nx,ny} can be associated with an area of 1, due to the fact that the point resides on a 1×1 area. **C.** Since the number of modes is the same as the area, the degeneracy can be calculated from the area of a quarder disk of radius n.

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:

$$\text{2D degeneracy(n)} = \left(\frac{1}{4}\right) 2\pi n \cdot \partial n$$

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:

$$\text{3D degeneracy(n)} = \left(\frac{1}{8}\right) 4\pi n^2 \cdot \partial n$$

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 λ, 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:

$$\text{3D degeneracy(n)} = \left(\frac{1}{8}\right) 4\pi \frac{4L^2}{\lambda^2} \cdot \partial n = \frac{2\pi L^2}{\lambda^2} \cdot \partial n$$

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: $\partial n \rightarrow \left|\frac{\partial n}{\partial \lambda}\right| \partial\lambda$:

$$\text{3D degeneracy}(\lambda) = 2 \times \frac{2\pi L^2}{\lambda^2} \cdot \left|\frac{\partial n}{\partial \lambda}\right| \partial\lambda = \frac{4\pi L^2}{\lambda^2} \left|\frac{\partial \frac{2L}{\lambda}}{\partial \lambda}\right| \partial\lambda = \frac{8\pi L^3}{\lambda^4}\, \partial\lambda$$

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 $\mathrm{k_B T}$.

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:

$$\text{Total Energy} = \sum_{\lambda} \text{degeneracy}(\lambda) \cdot \langle \text{energy}(\lambda) \rangle$$

Here we see that we need to calculate the average energy of the lightbulb's mode as a function of the mode's wavelength, $\langle \text{energy}(\lambda) \rangle$. We are already well aware that the energy of a photon is $\frac{\mathrm{h \cdot c}}{\lambda}$, 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 $\frac{\mathrm{h \cdot c}}{\lambda}$, 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:

$$\mathrm{P}\left(\frac{\mathrm{j \cdot h \cdot c}}{\lambda}\right) = \frac{\mathrm{e}^{-\text{Energy}/\mathrm{k \cdot T}}}{\sum \mathrm{e}^{-\text{Energy}/\mathrm{k \cdot T}}} = \frac{\mathrm{e}^{-\mathrm{j \cdot h \cdot c}/\lambda \cdot \mathrm{k_B T}}}{\sum_{\mathrm{i}=0}^{\infty} \mathrm{e}^{-\mathrm{i \cdot h \cdot c}/\lambda \cdot \mathrm{k_B T}}}$$

where $\mathrm{P}\left(\frac{\mathrm{j \cdot h \cdot c}}{\lambda}\right)$ 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), $\sum_{\mathrm{i}=0}^{\infty} \mathrm{e}^{-\mathrm{i \cdot h \cdot c}/\lambda \cdot \mathrm{k_B T}}$. 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:

$$\sum_{\mathrm{i}=0}^{\infty} \mathrm{a}^{\mathrm{i}} = \frac{1}{(1-\mathrm{a})}; \mathrm{i} = 0,1,2,3 \ldots$$

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: $\mathrm{a} = \mathrm{e}^{-\mathrm{h \cdot c}/\lambda \cdot \mathrm{k_B T}}$, which makes:

$$\sum_{\mathrm{i}=0}^{\infty} \mathrm{e}^{-\mathrm{i \cdot h \cdot c}/\lambda \cdot \mathrm{k_B T}} = \frac{1}{\left(1 - \mathrm{e}^{-\mathrm{h \cdot c}/\lambda \cdot \mathrm{k_B T}}\right)}$$

Now we can try to deal with the average energy via:

$$\langle\text{energy}\rangle = \sum \text{energy} \cdot \text{Boltzmann distribution}$$

$$= \sum_{j=0}^{\infty}\left(\frac{j\cdot h\cdot c}{\lambda}\right)\cdot\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)e^{-j\cdot h\cdot c/\lambda\cdot k_B T}$$

where: $\left(\frac{j\cdot h\cdot c}{\lambda}\right)$ is the energy of a j number of λ–wavelength photons and: $\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)e^{-j\cdot h\cdot c/\lambda\cdot k_B T}$ 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 $\sum_{j=0}^{\infty}\left(\frac{j\cdot h\cdot c}{\lambda}\right)\cdot e^{-j\cdot h\cdot c/\lambda\cdot k_B T}\cdot\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)$, we need to identify the constants: $\frac{h\cdot c}{\lambda}\cdot\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)$ and: $a = e^{-h\cdot c/\lambda\cdot k_B T}$. Thus, the average energy is:

$$\sum_{j=0}^{\infty}\left(\frac{j\cdot h\cdot c}{\lambda}\right)\cdot e^{-j\cdot h\cdot c/\lambda\cdot k_B T}\cdot\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right) = \left(\frac{h\cdot c}{\lambda}\right)\cdot e^{-h\cdot c/\lambda\cdot k_B T}\cdot\frac{\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)}{\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)^2}$$

This is:

$$\langle\text{energy}\rangle = \left(\frac{h\cdot c}{\lambda}\right)\cdot\frac{e^{-h\cdot c/\lambda\cdot k_B T}}{\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)}$$

Now we can simplify further by this neat trick of multiplying the top and bottom by $e^{h\cdot c/\lambda\cdot k_B T}$:

$$\left(\frac{h\cdot c}{\lambda}\right)\cdot\frac{e^{-h\cdot c/\lambda\cdot k_B T}}{\left(1-e^{-h\cdot c/\lambda\cdot k_B T}\right)}\cdot\frac{e^{h\cdot c/\lambda\cdot k_B T}}{e^{h\cdot c/\lambda\cdot k_B T}} = \left(\frac{h\cdot c}{\lambda}\right)\cdot\frac{e^0}{\left(e^{h\cdot c/\lambda\cdot k_B T}-e^0\right)} = \frac{h\cdot c}{\lambda\cdot\left(e^{h\cdot c/\lambda\cdot k_B T}-1\right)}$$

Done! The average energy of a λ-wavelength photon is:

$$\langle\text{energy}(\lambda)\rangle = \frac{h\cdot c}{\lambda\cdot\left(e^{h\cdot c/\lambda\cdot k_B T}-1\right)}$$

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.

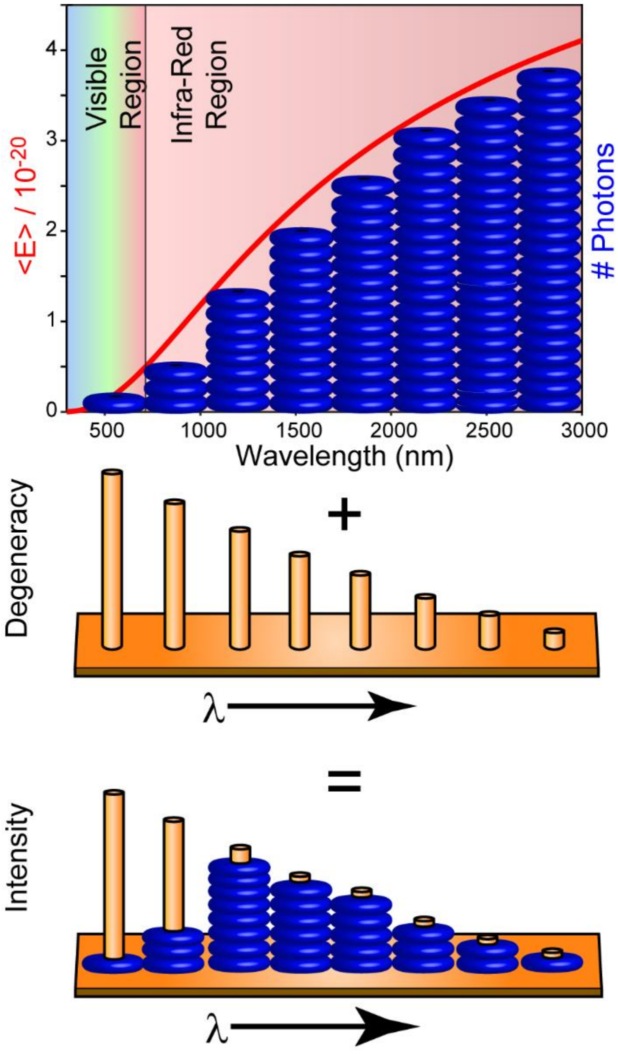


Figure 11.5. Stacking photon "disks" onto the allowed wavelength "posts" recreates the spectrum of the blackbody radiator.

Now to create a mathematical representation of the same. First, we return to our original expression for the total energy:

$$\text{Total Energy} = \sum_{\lambda} \text{degeneracy}(\lambda) \cdot \langle \text{energy}(\lambda) \rangle$$

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:

$$\text{Energy Density} = \frac{\text{Total Energy}}{\text{Volume}} = \frac{1}{L^3}\sum_{\lambda} \text{degeneracy}(\lambda) \cdot \langle \text{energy}(\lambda) \rangle$$

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:

$$\text{Energy Density} = \left(\frac{1}{L^3}\right)\int_0^{\infty}\left(\frac{8\pi L^3}{\lambda^4}\right) \cdot \frac{h \cdot c}{\lambda \cdot \left(e^{h \cdot c / \lambda \cdot k_B T} - 1\right)} \cdot \partial\lambda = \int_0^{\infty} \frac{8\pi \cdot h \cdot c}{\lambda^5 \cdot \left(e^{h \cdot c / \lambda \cdot k_B T} - 1\right)} \cdot \partial\lambda$$

where the expression:

$$\frac{8\pi \cdot h \cdot c}{\lambda^5 \cdot \left(e^{h \cdot c / \lambda \cdot k_B T} - 1\right)}$$

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

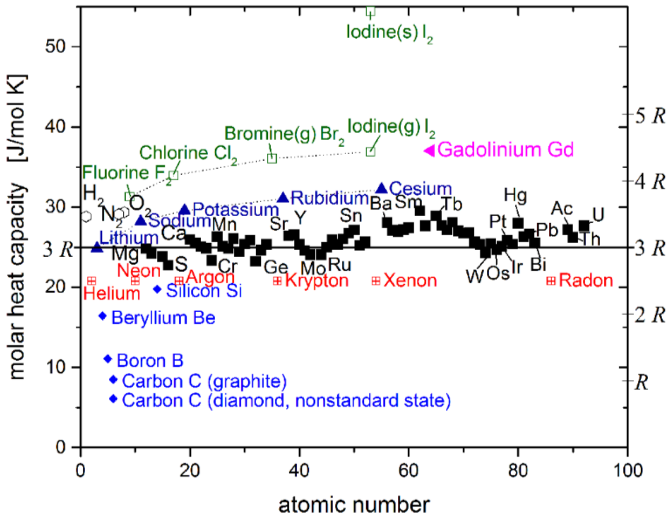


Figure 11.6. Per molar heat capacity of elements reveal clustering about the value 3R. Data from the CRC and wikipedia.

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.

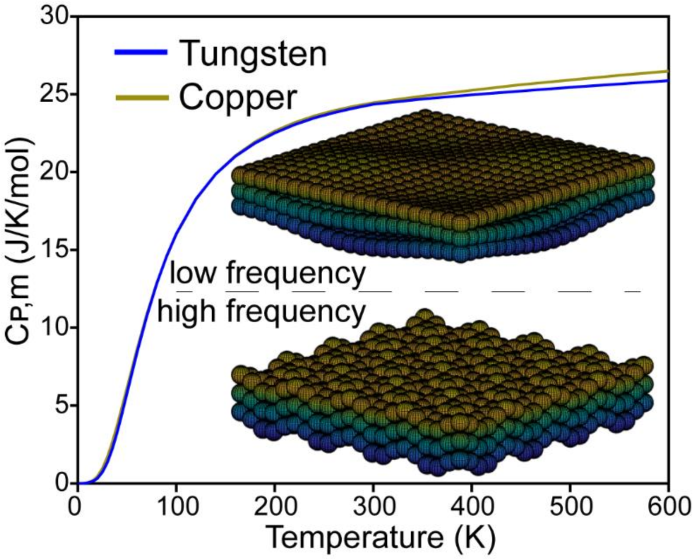


Figure 11.7. Temperature dependence of Cp,m of metals reveals a steep rise from 0 to ~3R near room temperature. Data from the CRC and wikipedia. Inset shows solid vibrations called phonons.

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: $\frac{\mathrm{h}\cdot \mathrm{c}/\lambda}{\mathrm{e}^{\hbar\cdot \mathrm{c}/\lambda \mathrm{k_B T}}-1} \rightarrow 3N_A \cdot \frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1}$. 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:

$$\mathrm{C} = 3\mathrm{N_A} \cdot \frac{\partial}{\partial \mathrm{T}}\left(\frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1}\right) = 3\mathrm{N_A} \cdot \frac{-\hbar\omega}{(\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1)^2}\frac{\partial \mathrm{e}^{\hbar\omega/\mathrm{k_B T}}}{\partial \mathrm{T}}$$

$$= 3\mathrm{N_A} \cdot \frac{-\hbar\omega}{(\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1)^2}\frac{-\hbar\omega}{\mathrm{k_B T}^2}\mathrm{e}^{\hbar\omega/\mathrm{k_B T}} = 3\mathrm{N_A k_B}\left(\frac{\hbar\omega}{\mathrm{k_B T}}\right)^2 \frac{\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}}{(\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1)^2}$$

This result correctly predicts that, as T→0 K, the heat capacity also →0 J/K/mol. At higher temperatures where: $\mathrm{e}^{\hbar\omega/\mathrm{k_B T}} \sim 1 + \frac{\hbar\omega}{\mathrm{k_B T}}$ we find that:

$$\mathrm{C}\sim 3\mathrm{N_A k_B}\left(\frac{\hbar\omega}{\mathrm{k_B T}}\right)^2 \frac{1+\frac{\hbar\omega}{\mathrm{k_B T}}}{\left(\frac{\hbar\omega}{\mathrm{k_B T}}\right)^2} \sim 3\mathrm{N_A k_B}\left(\frac{\hbar\omega}{\mathrm{k_B T}}\right)^2 \left(\frac{\mathrm{k_B T}}{\hbar\omega}\right)^2 = 3\mathrm{N_A k_B} = 3\mathrm{R}$$

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 $C_{p,m}\sim T^3$ 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:

$$\mathrm{U} = \int \mathrm{degeneracy}(\omega)\cdot\langle\mathrm{energy}(\omega)\rangle = \int \mathrm{degeneracy}(\omega)\cdot\frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1}\partial\omega$$

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:

$$\mathrm{C} = \frac{\partial \mathrm{U}}{\partial T} = \frac{\partial}{\partial T}\frac{V\omega^2}{2\pi^2 v_s^3}\int_0^{\omega_D}\frac{V\omega^2}{2\pi^2 v_s^3}\frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/\mathrm{k_B T}}-1}\partial\omega \propto T^3$$

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

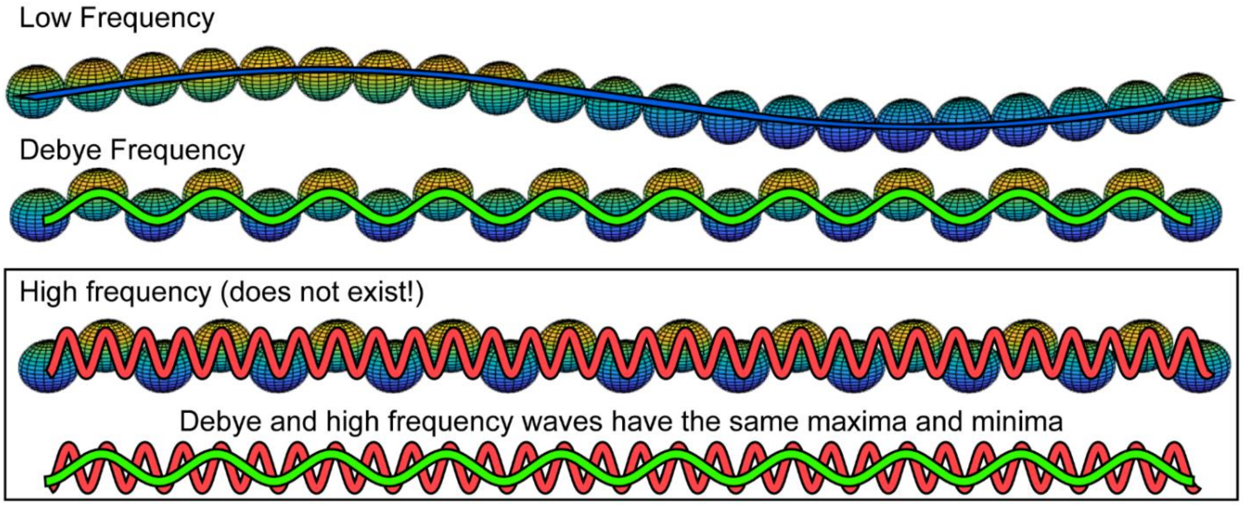


Figure 11.8. Phonons have an upper (Debye) phonon frequency limit as defined by the distance between neighboring atoms. This is because there is no practical difference between the Debye frequency and a shorter wavelength phonon as shown on the bottom.

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.

Problems: Numerical

1. a. Write Plank's constant ($h=6.626\times10^{-34}$ J·s) in units of kg, m, and s. **(2 pts)**

b. What are the unit(s) of $c\cdot h/\lambda$? **(2 pts)**

c. What are the unit(s) of momentum squared over mass? **(2 pts)**

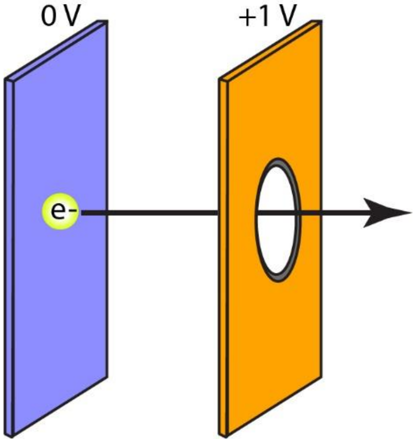
d. What are the unit(s) of Plank's constant squared over mass over length squared? **(2 pts)**

2. a. What is the de Broglie wavelength of Donald Trump, a 210 kg man who can run 1.0 m/s when chased by a mob at the Capitol? **(3 pts)**

b. What was the de Broglie wavelength of Secretariat, a 544 kg horse that could run 21.9 m/s? I'm using the past tense because the horse is dead. He's **dead**. **(3 pts)**

3. a. What is the de Broglie wavelength of Ted Cruz, a 100 kg man who can run 0.5 m/s when chased by a mob at the Capitol? **(3 pts)**

b. What was the de Broglie wavelength of Secretariat, a 544 kg horse that could run 21.9 m/s? I'm using the past tense because the horse is dead. He's **dead**. **(3 pts)**



4. Let's learn about a new unit- the electron Volt (eV). This is the energy an electron picks up by travelling across two metal plates, one at 0 V and the other at +1.0 V. The electron will accelerate towards the +1.0 V, picking up kinetic energy. Actually, it picks up 1.0 eV of kinetic energy to be exact! (rest mass of an electron is $m_0 = 9.109\times10^{-31}$ kg and the speed of light is $c=3\times10^{8}$ m/s).

a. If the conversion of J to eV is $1.6\times10^{-19}\ (^{J}/_{eV})$, how fast is an electron going once it passes through a +1.0 V plate? **(3 pts)**

b. What is interesting is that the mass of an electron is dependent on how fast it is moving (thanks Einstein!) If the mass of the moving particle is: $m = \left(1-\frac{v^2}{c^2}\right)^{-1/2}\cdot m_0$, where c is the speed of light and m_0 is the "rest mass" of the electron (9.109×10^{-31} kg), does the mass of the 1 eV electron change much? **(3 pts)**

c. What speed would an electron have to travel to have a mass that is 10% higher than its rest mass? How many eV is that? **(7 pts)**

Hint: for pt. c if you calculated 44.5 keV you forgot to account for the mass increase.

5. The length between chemical bonds is ~1 Å. To perform diffraction studies on bonds, you would practically need to use a particle with a wavelength that is about 1/100th this value, i.e. 1×10^{-12} m.

a. What speed do you need to make electrons travel at to give them this wavelength such that they can be used in diffraction experiments for elucidating the structure of molecules? ***Hint:*** $\lambda = \frac{h}{m \cdot v}$. Also the electron rest mass is 9.109×10^{-31} kg. **(3 pts)**

b. Look really closely at your answer to pt. a, and you will find that there is a major problem with the speed you calculated. What it wrong with it? **(2 pts)**

c. Now if an electron is travelling 2.77×10^{8} m/s (which is less than the speed of light) and the mass increases according to: $m = \left(1 - \frac{v^2}{c^2}\right)^{-1/2} \cdot m_0$, what is the de Broglie wavelength of the particle travelling at this speed?

(5 pts)

Problems: Theoretical or Explain in Words

1. The correct equation that Einstein derived for the energy from the theory of relativity is not $E=mc^2$, rather $E^2=p^2 \cdot c^2 + m^2 \cdot c^4$ (m is mass, c is the speed of light).

a. What assumption allows you to say $E=m \cdot c^2$? **(2 pts)**

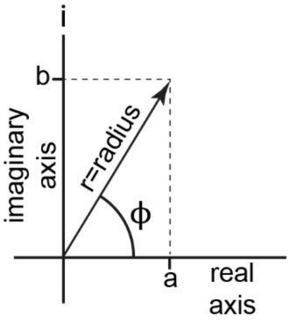
b. If energy of light is $E=c \cdot h/\lambda$, can you derive what the momentum of light is, i.e. p = ? **(3 pts)**

pt. b. hint: photons have no mass, so $E^2 = p^2 \cdot c^2$

2. A complex number is defined as having $\sqrt{-1}$ in it, where we abbreviate $i = \sqrt{-1}$. Hence "3i" is a complex number, and $(3i)^2 = 3^2 \cdot i^2 = -9$. A complex number can generally be expressed as: $z = a + i \cdot b$. Its absolute value $|z|$ is: $|z| = \sqrt{a^2 + b^2}$; it works just like a vector!

Last thing, the complex conjugate of z, which we call z^*, is defined as: $z^* = a - i \cdot b$.

a. Can you prove that, for $z = a + i \cdot b$, then $z^* \cdot z = |z|^2$? **(3 pts)**



b. Let's make an equivalency between $z = a + i \cdot b$ and $z = |r| \cdot e^{i\phi}$ using the figure provided here. To answer this question, please define $|r|$ and ϕ using a and b. FYI, the purpose of this question is to make you comfortable with Googling math identities. **(3 pts)**

c. Please use the FOIL method to evaluate: $z^2 = (a + i \cdot b)^2$. **(3 pts)**

d. If you had to evaluate z^{50}, which representation of z (i.e., $z = a + i \cdot b$ or $z = |r| \cdot e^{i\phi}$) would you use and why?

(3 pts)

3. More math practice. A complex function ψ has "i" in it, and the complex conjugate of ψ is the same thing where every "i" is replaced with "-i". For example, if $\psi(x) = i \cdot \sin(-i \cdot kx)$, then $\psi^*(x) = -i \cdot \sin(i \cdot kx)$. Here is another: $-i^* = -(-i) = i$.

a. If $\psi(\phi) = \sin(\phi)$, what is $\psi(\phi) \cdot \psi^*(\phi)$? **(3 pts)**

b. If $\psi(\phi) = e^{i\phi}$, what is $\psi(\phi) \cdot \psi^*(\phi)$? Please simplify the product and provide one answer.

(fyi $e^a e^b = e^{a+b}$) **(3 pts)**

c. If $\psi(\phi) = e^{i\phi} \cdot \sin(\phi)$, what is $\psi(\phi) \cdot \psi^*(\phi)$? **(3 pts)**

4. More math practice. A complex function ψ has "i" in it, and the complex conjugate of ψ is the same thing where every "i" is replaced with "-i". For example, if $\psi(x) = i \cdot \sin(-i \cdot kx)$, then $\psi^*(x) = -i \cdot \sin(i \cdot kx)$. You see, everywhere the "i" appeared, we wrote "-i" instead. Here is another: –i* = –(-i) = i.

a. If $\psi(\phi) = \cos(\phi)$, what is $\psi(\phi) \cdot \psi^*(\phi)$? **(3 pts)**

b. If $\psi(\phi) = e^{i\phi}$, what is $\psi(\phi) \cdot \psi^*(\phi)$? Please simplify the product and provide one answer.

(fyi $e^a e^b = e^{a+b}$) **(3 pts)**

c. If $\psi(\phi) = e^{i\phi} \cdot \cos(\phi)$, what is $\psi(\phi) \cdot \psi^*(\phi)$? **(3 pts)**

5. Even more math practice! Perform the following operations. Oh, I'm sorry I didn't say that right. Perform the following operations please.

a. $\frac{\partial}{\partial x} \cdot \frac{\partial}{\partial x} \cdot x \cdot \cos(kx)$ **b.** $\frac{\partial}{\partial x} \cdot x \cdot \frac{\partial}{\partial x} \cdot \cos(kx)$ **c.** $\frac{\partial}{\partial x} \cdot \frac{1}{x} \cdot \frac{\partial}{\partial x} \cdot e^{i \cdot k \cdot x}$ **(9 pts)**

Hint: Look at some of the identities at the top of the problem set!

6. Even more math practice! Perform the following operations. Oh, I'm sorry I didn't say that right. Perform the following operations please.

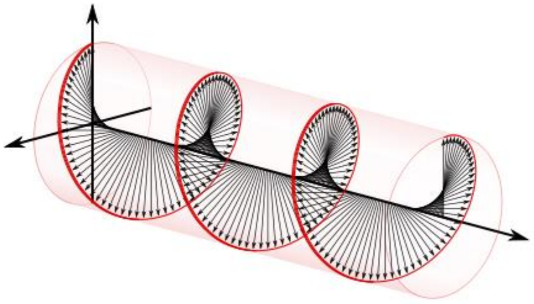
a. $\frac{\partial}{\partial x} \cdot \frac{\partial}{\partial x} \cdot x \cdot \sin(kx)$ **b.** $\frac{\partial}{\partial x} \cdot x \cdot \frac{\partial}{\partial x} \cdot \sin(kx)$ **c.** $\frac{\partial}{\partial x} \cdot \frac{1}{x} \cdot \frac{\partial}{\partial x} \cdot e^{-i \cdot k \cdot x}$ **(9 pts)**

7. Light has two "natural" forms- right and left circularly polarized. This comes about because light has angular momentum, specifically ℓ = 1, where ℓ is the angular momentum quantum state (like how the hydrogen s-state has ℓ = 0 and p states have ℓ =1, remember this?). This is why the selection rule □ℓ = ±1 for absorption of light exists (i.e. why s-states absorb light and turn into p-states; this conserves angular momentum!). Here is another fact: if ℓ > 0, then there are 2ℓ + 1 "sub" quantum states m_ℓ that range from: m_ℓ = {-ℓ, (-ℓ +1), …, 0, …, +ℓ} (you learned this in Freshman Chem). For a hydrogen p-state with quantum state ℓ =1, you have three m_ℓ = {-1, 0, 1} states, which is where the three p_x, p_y, and p_z orbitals come from!

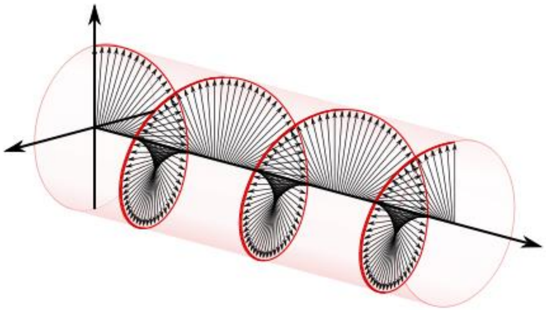
If light has angular momentum and is in quantum state ℓ =1, then there must be three m_ℓ = {-1, 0, +1} states. Actually, there are, but just two of them- specifically, m_ℓ = +1, which is what we call left circularly polarized light, and m_ℓ = -1, which is right circularly polarized light. **But there is no m_ℓ = 0 state!**

Now here is the question- why is that the case? Here are two figures for right and left circularly polarized light that will help you, where you can see how the electric field rotates around the axis of propagation: **(5 pts)**

Right:



Left:



Hint: In the $m_\ell = 0$ case, the photon rotates by moving forward and backward in line with the direction of propagation.

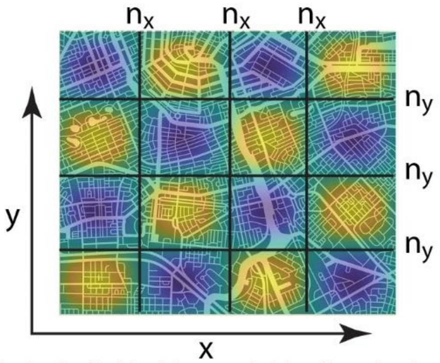
8. The solution to Ampere's Law in 3D: $\frac{\partial^2 \vec{E}}{\partial x^2} + \frac{\partial^2 \vec{E}}{\partial y^2} + \frac{\partial^2 \vec{E}}{\partial z^2} = \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2}$ is: $\vec{E} = f(x) \cdot f(y) \cdot f(z) \cdot f(t)$,

where the time dependent function is: $f(t) = \sin\left(2\pi \cdot c \cdot \frac{t}{\lambda}\right)$

a. What does c·t represent? **b.** What are the units of $c \cdot \frac{t}{\lambda}$? **c.** Why is there a 2π?

d. Now, summarize why the argument of the sine function: $2\pi \cdot c \cdot \frac{t}{\lambda}$ makes sense. **(8 pts)**

9. Here we will calculate the population distribution of COVID patients as a function of the number of low-income citizens (NP). The map shown here will help you understand the variables.



A city is divided into neighborhoods via the n_x and n_y boundaries. The wealthy and low-income areas have different numbers of COVID patients and hospital bed availabiltiy.

a. First, it is determined that the number of COVID cases changes with the geographic location (**x**, **y**), the population (**pop**), area A and number of low-income people (NP) according to the following:

$$\text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop}) = f(\mathbf{x}) \cdot f(\mathbf{y}) \cdot f(\mathbf{pop})$$
$$= \sin\left(\frac{n_x \pi}{\sqrt{A}} \cdot \mathbf{x}\right) \cdot \sin\left(\frac{n_y \pi}{\sqrt{A}} \cdot \mathbf{y}\right) \cdot \sin\left(\frac{2\pi}{NP} \cdot \mathbf{pop}\right)$$

Here, n_x and n_y represent the number of boundaries between the rich and poor neighborhoods. The function $\text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop})$ is the solution to the following differential equation:

$$\frac{\partial^2}{\partial \mathbf{x}^2}\text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop}) + \frac{\partial^2}{\partial \mathbf{y}^2}\text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop}) = \frac{\partial^2}{\partial \mathbf{pop}^2}\text{Cases}(\mathbf{x}, \mathbf{y}, \mathbf{pop})$$

Please use this differential equation and the formula for Cases to demonstrate: **(7 pts)**

$$n_x^2 + n_y^2 = \frac{4 \cdot A}{NP^2}$$

Hint: the first term is: $\frac{\partial^2 \text{Cases}}{\partial \mathbf{x}^2} = \frac{\partial^2 \sin\left(\frac{n_x \pi}{\sqrt{A}} \cdot \mathbf{x}\right)}{\partial \mathbf{x}^2} \cdot f(\mathbf{y}) \cdot f(\mathbf{pop}) = -\left(\frac{n_x^2 \pi^2}{A}\right) \cdot f(\mathbf{x}) \cdot f(\mathbf{y}) \cdot f(\mathbf{pop})$

b. We can simplify the result from pt. a: $n_x^2 + n_y^2 = \frac{4 \cdot A}{NP^2}$ as: $n^2 = \frac{4 \cdot A}{NP^2}$. Next, we learn from the County Health office that the number of hospital beds available to the population is:

$$\text{Beds}(n) = \left(\frac{1}{4}\right) 2\pi n \cdot \partial n$$

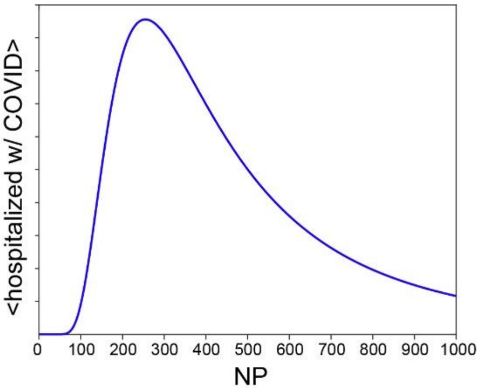
Can you convert this into the number of beds available as a function of the size of the low-income population? Meaning, convert Beds(n) into Beds(NP) given that $n^2 = \frac{4 \cdot A}{NP^2}$? **(7 pts)**

Hint: You need to use a Jacobian: $\partial n = \left|\frac{\partial n}{\partial NP}\right| \partial NP$.

c. When you multiply the number of available hospital beds: Beds(NP) with the average number of COVID patients as a function of the size of the low-income population: $\langle P(NP) \rangle = \frac{1}{NP \cdot \left(e^{1000/NP} - 1\right)}$ you arrive at the COVID patient distribution:

$$\text{Beds}(NP) \cdot \langle P(NP) \rangle = \frac{2\pi \cdot A}{NP^3} \frac{1}{NP \cdot \left(e^{1000/NP} - 1\right)} \partial NP = \frac{2\pi \cdot A}{NP^4 \left(e^{1000/NP} - 1\right)} \partial NP$$

A graph of the above distribution is shown. Can you describe why the graph rises and falls as it does? Please explain the answer as though you were speaking to a middle school student. For example, don't you already know how COVID affects low-income earners disproportionately? What kind of access to medical care to low-income people have? Discuss how these are related to the equations developed. **(5 pts)**

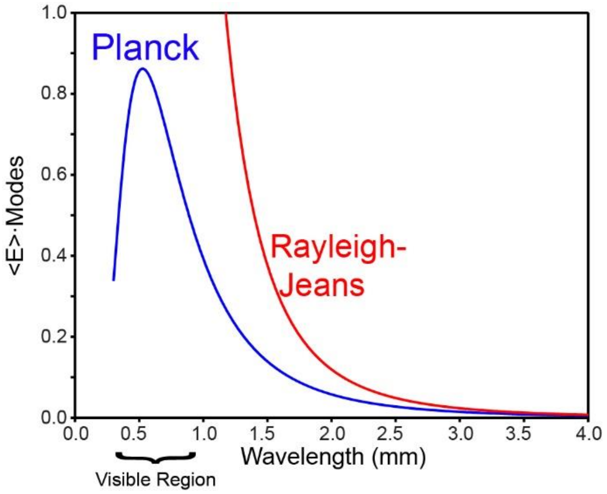


d. What would integrating the result in pt. c yield? Note you don't have to actually integrate it, just describe what the numerical result would mean as though you were speaking to a middle school student. **(3 pts)**

10. Now let's repeat what we did with problem #9 for lightbulbs. We determined that the Boltzmann equation's normalizer for the blackbody radiator problem is:

$$\text{Norm} = \left\{1 - e^{\frac{-hc}{\lambda \cdot k_B T}}\right\}^{-1}$$

Please evaluate $(k_B T)^2 \frac{\partial \ln(\text{Norm})}{\partial (k_B T)}$ to show that it is the same as the average energy. **(10 pts)**



Hint: You have the correct equation for the average energy from class and Ch. 12 of "Free Energy". Also you will need to use the following identity: $\frac{\partial}{\partial x}\ln\left(1-e^{\frac{-a}{x}}\right)=-\frac{a}{x^2\left(e^{\frac{a}{x}}-1\right)}$

11. When people were first working on the blackbody radiator problem they thought to use the Equipartition theorem to calculate the energy of a photon:

$$\langle E\rangle=\frac{k_B T}{2}\cdot \text{degrees of freedom}$$

The number of degrees of freedom is 2 for a photon because they can be left- or right-circularly polarized. Consequently, the blackbody intensity distribution would be:

$$\text{Modes}(\lambda)\cdot\langle E\rangle=\frac{8\pi L^3}{\lambda^4}\cdot k_B T\cdot\partial\lambda$$

This is called the Rayleigh-Jeans law, which isn't correct as can be demonstrated by calculating the total energy output of the object via integration:

$$Total\ energy=\int_0^\infty \frac{8\pi L^3}{\lambda^4}\cdot k_B T\cdot\partial\lambda$$

a. What do you get when you evaluate $\int_0^\infty \frac{8\pi L^3}{\lambda^4}\cdot k_B T\cdot\partial\lambda$? **(3 pts)**

You may need to use an on-line integrator:

https://www.wolframalpha.com/widgets/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605

FYI, if the on-line thing states "does not converge", then the answer is ∞.

b. The problem encountered with the answer with pt. a was called the "Ultraviolet Catastrophe". Why do you think they called the result that? **(3 pts)**

12. There is an idea that quantum mechanical expressions should turn into classical ones under some limit. For example, the quantum Planck distribution: $\frac{8\pi L^3}{\lambda^5}\cdot\frac{hc}{\left(e^{hc/\lambda k_B T}-1\right)}$ should turn into the classical Rayleigh-Jeans one: $\frac{8\pi L^3}{\lambda^4}\cdot k_B T$. But how?

a. First, look at the $e^{hc/\lambda k_B T}$ term, and use this identity: $e^x=1+x+\frac{x^2}{2!}+\frac{x^3}{3!}$... to simplify it to the 2nd term (i.e. do this: $e^x\approx 1+x$). This simplification is valid if λ is very very long. **(7 pts)**

b. Now plug in your answer above into $\frac{8\pi L^3}{\lambda^5}\cdot\frac{hc}{\left(e^{hc/\lambda k_B T}-1\right)}$ and simplify it- what do you have? **(7 pts)**

c. What one finds is that all quantum mechanical equations have "h" in them, but classical equations never do. Thus, the Rayleigh-Jeans law is "classical" because it doesn't have Planck's constant. It also correctly describes the lightbulb for long wavelengths, but not short ones as shown here. Now, you may be wondering what the question is. There isn't one- did you notice how many points this question is worth? **( pts)**

Chapter 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, $\mathrm{E} = \mathrm{mc}^2$ anyone? Not hardly, Einstein derived the following:

$$\mathrm{E}^2 = \mathrm{c}^2\mathrm{p}^2 + \mathrm{m}^2\mathrm{c}^4$$

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 $\mathrm{E}^2 = \mathrm{m}^2\mathrm{c}^4$ which simplifies to:

$$\mathrm{E} = \mathrm{mc}^2$$

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 ($\mathrm{m} = 0$ kg). In that case:

$$\mathrm{E}^2 = \mathrm{c}^2\mathrm{p}^2 \rightarrow \mathrm{E} = \mathrm{cp}$$

The energy of a photon is known to be hυ, where h is Planck's constant and υ is frequency which is: $\upsilon = \frac{\mathrm{c}}{\lambda}$ and λ is the wavelength. We can thus show that $\mathrm{E} = \mathrm{h}\frac{\mathrm{c}}{\lambda} = \mathrm{cp}$, which means that a massless particle such as a photon has a momentum: $\mathrm{p} = \frac{\mathrm{h}}{\lambda}$. 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:

$$\nabla \times \mathcal{E} = -\frac{\partial \mathrm{B}}{\partial \mathrm{t}}$$

$$\nabla \times \mathrm{B} = \frac{1}{\mathrm{c}^2}\frac{\partial \mathcal{E}}{\partial \mathrm{t}}$$

$$\nabla \mathcal{E} = 0$$

$$\nabla \mathrm{B} = 0$$

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:

$$\frac{\partial^2}{\partial \mathrm{x}^2}\mathcal{E} = \frac{1}{\mathrm{c}^2}\frac{\partial^2}{\partial \mathrm{t}^2}\mathcal{E}$$

A function for the electric field $\mathcal{E}$ that can solve the above is: $\mathcal{E}(\mathrm{x},\mathrm{t}) = \cos\left(\frac{2\pi}{\lambda}\mathrm{x} - \omega \mathrm{t}\right)$, where ω is the angular frequency ($\omega = 2\pi\nu$). This describes a wave travelling to the right. If we input this function into: $\frac{\partial^2}{\partial \mathrm{x}^2}\mathcal{E} = \frac{1}{\mathrm{c}^2}\frac{\partial^2}{\partial \mathrm{t}^2}\mathcal{E}$, and by calculating the double derivatives we can show that:

$$\frac{\partial^2}{\partial \mathrm{x}^2}\cos\left(\frac{2\pi}{\lambda}\mathrm{x} - \omega \mathrm{t}\right) = \frac{1}{\mathrm{c}^2}\frac{\partial^2}{\partial \mathrm{t}^2}\cos\left(\frac{2\pi}{\lambda}\mathrm{x} - \omega \mathrm{t}\right)$$

And therefore:

$$\left(\frac{2\pi}{\lambda}\right)^2 \cos\left(\frac{2\pi}{\lambda}\mathrm{x} - \omega \mathrm{t}\right) = \frac{\omega^2}{\mathrm{c}^2}\cos\left(\frac{2\pi}{\lambda}\mathrm{x} - \omega \mathrm{t}\right)$$

Since you can eliminate the function $\cos\left(\frac{2\pi}{\lambda}\mathrm{x} - \omega \mathrm{t}\right)$ from both sides the remainder is: $\left(\frac{2\pi}{\lambda}\right)^2 = \frac{\omega^2}{\mathrm{c}^2}$, and thus $\lambda\omega = 2\pi \mathrm{c}$. This is a well-known description of how wavelength and frequency of light are related.

Travelling vs. Standing waves

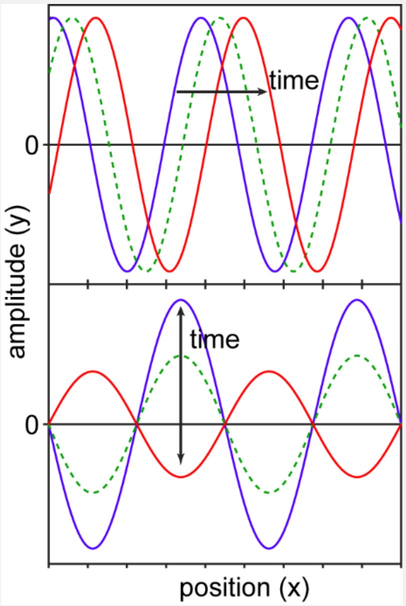
Equations such as:

$$\cos\left(2\pi \cdot \frac{x}{\lambda} - \omega \cdot t\right)$$

represent travelling waves, which is obvious if you look at a figure of this function over time as shown below (top). The above example is for a wave moving to the right. However, you are also aware of standing waves, you probably created one when you shook a rope up and down at the right frequency. The reason a standing wave forms is that the waves you input reflect off the end and travel back to you. The addition of the left and right moving waves:

$$\cos\left(2\pi \cdot \frac{x}{\lambda} - \omega \cdot t\right) + \cos\left(2\pi \cdot \frac{x}{\lambda} + \omega \cdot t\right) =$$
$$2 \cdot \cos\left(2\pi \cdot \frac{x}{\lambda}\right) \cdot \sin(\omega \cdot t)$$

creates the standing wave as shown on the bottom of the figure . In quantum mechanics we have both types, where a travelling wave carries energy with it like an electron shot out of a hot wire filament. A standing wave represents a quantum entity that is sitting "still". An example is the hydrogen atom, which has an electron that cannot "escape" because it remains bound to the nucleus by the Coulombic interaction.



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 hν 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 $\psi(x,t)$ 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:

$$\text{Kinetic Energy} + \text{Potential Energy} = \text{Total Energy}$$

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 $h\upsilon$ of a wave:

$$mc^2 = h\upsilon$$

As the frequency of light υ is related to the wavelength by: $\lambda\upsilon = c$, the energy of the wave can be converted into: $h\upsilon = h\frac{c}{\lambda}$. 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

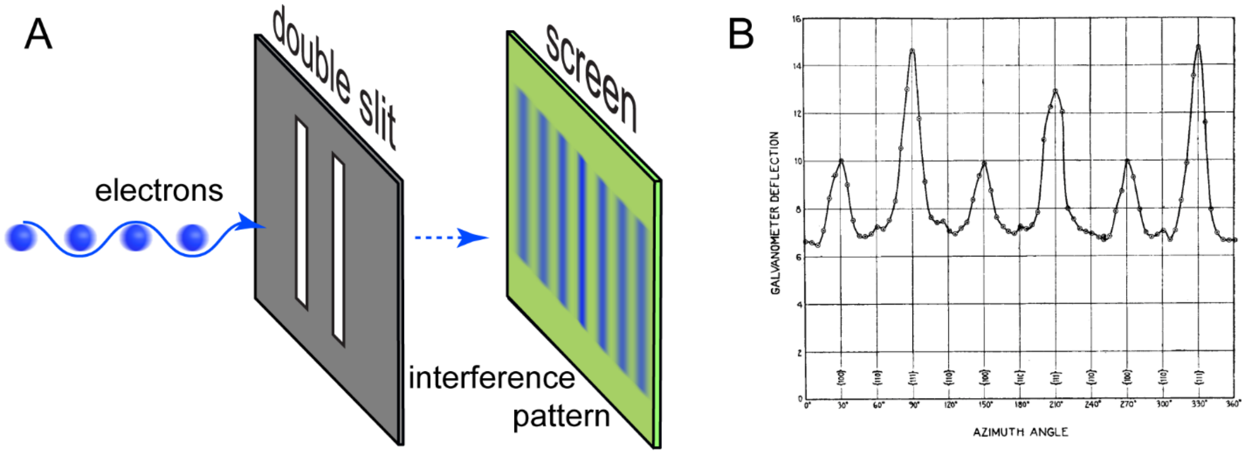


Figure 12.1. A. Davisson and Germer discovered that electrons can diffract through a material and create a diffraction pattern, proving that matter has wave like properties. **B.** Davisson and Germer's original data from 1927.

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 $\mathrm{k} = \frac{2\pi}{\lambda}$, 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:

$$\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\psi = \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\cos(\mathrm{kx}) = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}\cos(\mathrm{kx}) = \mathrm{E}\cdot\cos(\mathrm{kx})$$

From the above it must be true that: $\frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}} = \mathrm{E}$, and as a result: $\mathrm{k} = \frac{\sqrt{2\mathrm{mE}}}{\hbar}$ and $\psi = \cos\left(\frac{\sqrt{2\mathrm{mE}}}{\hbar}\mathrm{x}\right)$. You may also notice from the above that: $\mathrm{p}^2 = \hbar^2\mathrm{k}^2$, and since $\mathrm{k} = \frac{2\pi}{\lambda}$ and $\hbar = \frac{\mathrm{h}}{2\pi}$ we have: $\mathrm{p}^2 = \left(\frac{\mathrm{h}}{2\pi}\right)^2\left(\frac{2\pi}{\lambda}\right)^2$ which simplifies to the de Broglie relationship: $\lambda = \frac{\mathrm{h}}{\mathrm{p}}$. 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?

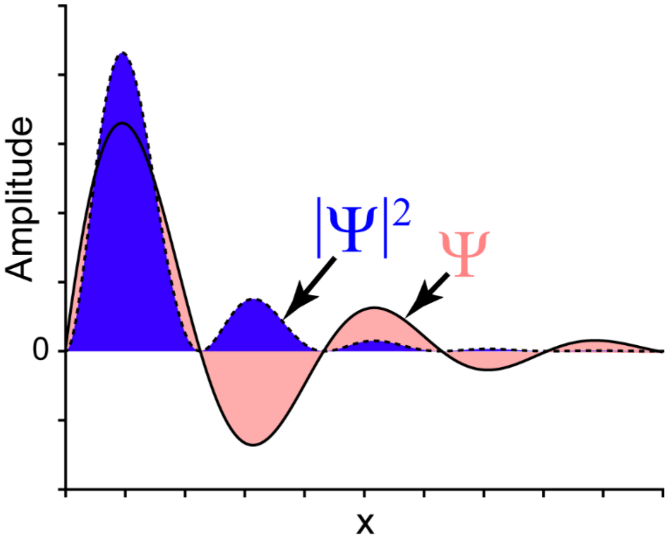


Figure 12.2. The Born interpretation is that the absolute value of a wavefunction |Ψ|² is a probability density.

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:

$$\int_{\text{lower limit}}^{\text{upper limit}} |\psi|^2\,\partial\tau = \int_{\text{lower limit}}^{\text{upper limit}} \psi^*\psi\,\partial\tau = 1.0$$

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:

$$\psi_{\text{norm}} = N\psi = \frac{1}{\sqrt{\int|\psi|^2\,\partial\tau}}\psi$$

As a result:

$$\int \psi_{\text{norm}}^2\,\partial\tau = \frac{\int \psi^*\psi\,\partial\tau}{\sqrt{\int|\psi|^2\,\partial\tau}\sqrt{\int|\psi|^2\,\partial\tau}} = \frac{\int \psi^*\psi\,\partial\tau}{\int \psi^*\psi\,\partial\tau} = 1$$

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.

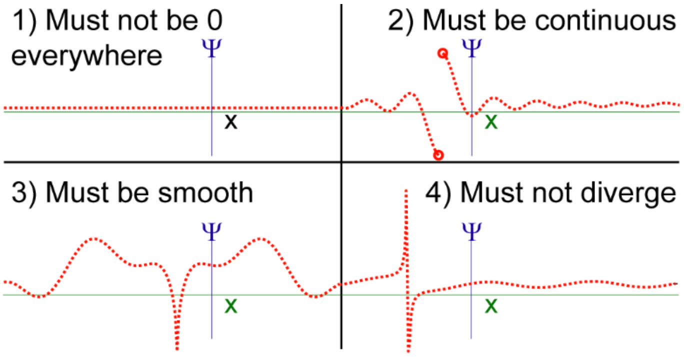


Figure 12.3. Quantum mechanical wavefunctions must follow the rules shown here to properly behave according to the rules of probability.

12.4 The Eigenvalue Equation and operators.

Previously we

referred to the kinetic energy part: $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}$ 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: $\widehat{\Omega}$, where the "hat" signifies a quantum mechanical operator. We will use the Φ symbol for the wave equation that $\widehat{\Omega}$ operates on (and unfortunately Φ 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: $\widehat{\Omega} = \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}$ to the wave equation: $\Phi = \cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right)$ that we were able to calculate the energy via what is called the "eigenvalue equation":

$$\widehat{\Omega}\Phi = \omega\Phi$$

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 Φ 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 $\widehat{\Omega}$ that acts on $\Phi = \mathrm{N}\cdot\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right)$ as follows:

$$\widehat{\Omega}\Phi = \widehat{\Omega}\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right) = \frac{2\pi}{\lambda}\cdot\sin\left(\frac{2\pi}{\lambda}\mathrm{x}\right) \neq \omega\Phi \quad \text{or} \quad \widehat{\Omega}\Phi = \widehat{\Omega}\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right) = \mathrm{x}\cdot\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right) \neq \omega\Phi$$

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 Φ is an eigenfunction of the operator $\widehat{\Omega}$. To verify our understanding, we will measure the kinetic energy once again:

$$\widehat{\Omega}\Phi = \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right)\omega\Phi = \frac{2\pi^2\hbar^2}{\mathrm{m}\lambda^2}\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right) = \omega\Phi$$

Complex mathematics

Despite the name, complex mathematics is not that hard. It's all about the letter "i", which is equal to $\sqrt{-1}$. As a result, $i^2 = -1$. Likewise: $i^3 = -i$ and $i^4 = 1$. Here are some additional indentities:

If: $e^x = 1 + x + \frac{x^2}{2} + \frac{x^3}{6} + \frac{x^4}{24} + \frac{x^5}{120}$ ...

therefore: $e^{ix} = 1 + ix + \frac{i^2x^2}{2} + \frac{i^3x^3}{6} + \frac{i^4x^4}{24} + \frac{i^5x^5}{120} + \cdots$

If you separate real from imaginary: $e^{ix} = \left(1 - \frac{x^2}{2} + \frac{x^4}{24}\right) + i\left(x - \frac{x^3}{6} + \frac{i^5x^5}{120}\right) + \cdots$, and from what you might recall of $\cos(x) = 1 - \frac{x^2}{2} + \frac{x^4}{24}$ ... and $\sin(x) = x - \frac{x^3}{6} + \frac{i^5x^5}{120}$ ... you can show:

$$e^{ix} = \cos(x) + i \cdot \sin(x)$$

Likewise, $e^{-ix} = \cos(x) - i \cdot \sin(x)$. These relationships can be combined into:

$$\sin(x) = \frac{e^{ix} - e^{-ix}}{2i} \text{ and } \cos(x) = \frac{e^{ix} + e^{-ix}}{2}$$

Another valuable relationship is the complex conjugate, which is $\psi^*(i) = \psi(i)$. Therefore $\psi^2 = \psi^*\psi$. Here is an example, if $\psi = e^{ikx} = \cos(kx) + i \cdot \sin(kx)$ and $\psi^* = \cos(kx) - i \cdot \sin(kx)$, then it is easy to show that:

$$\psi^*\psi = \cos(kx) + i \cdot \sin(kx)\big(\cos(kx) - i \cdot \sin(kx)\big) =$$

$$\cos^2(kx) - i \cdot \cos(kx)\sin(kx) + i \cdot \cos(kx)\sin(kx) + \sin^2(kx) = 1$$

A graph of $\psi = e^{ikx}$ is shown here. Note how the real and imaginary parts of the function have to be graphed separately.

This is a good example, and we know that the kinetic energy of the particle that is described by the wave equation $\Phi = \cos\left(\frac{2\pi}{\lambda}x\right)$ 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 Φ are eigenfunctions of the operator $\widehat{\Omega}$".

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 $\widehat{H}$; 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

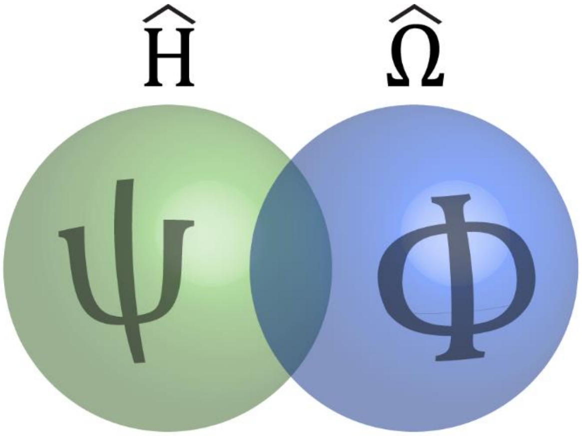


Figure 12.4. Eigenfunctions of one operator may, nor may not be eigenfunctions of another operator.

back to the example of a Hamiltonian operator with no potential energy, i.e. $\widehat{\mathrm{H}} = \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}$. A wavefunction of this Hamiltonian is $\psi = \cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right)$, and has an energy as we showed on the previous page. Now, if we apply the momentum operator to the same state:

$$\hat{\mathrm{p}}\psi = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \mathrm{x}}\cos\left(\frac{2\pi}{\lambda}\mathrm{x}\right) = \frac{-2\pi\hbar}{\mathrm{i}\lambda}\cdot\sin\left(\frac{2\pi}{\lambda}\mathrm{x}\right) \neq \omega\psi$$

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: $\psi = \mathrm{N}\cdot\cos(\mathrm{kx})$ where N is the normalization constant and $\mathrm{k} = \frac{2\pi}{\lambda}$ 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. $\widehat{\mathrm{V}} = 0$) Hamiltonian:

$$\widehat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\{\mathrm{N}\cdot\cos(\mathrm{kx})\} = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial}{\partial \mathrm{x}}\{\mathrm{N}\cdot\mathrm{k}\cdot\sin(\mathrm{kx})\} = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}\{\mathrm{N}\cdot\cos(\mathrm{kx})\}$$

Comparison to the eigenvalue equation $\widehat{\mathrm{H}}\psi = \mathrm{E}\psi$ reveals that the above is in the proper form, so we can be sure that the energy is: $\frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}$.

Now let's repeat the above using the complex mathematical version of the wavefunction, i.e. $\psi = \mathrm{N}\cdot\cos(\mathrm{kx}) = \mathrm{N}\cdot\left(\frac{1}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{1}{2}\mathrm{e}^{-\mathrm{ikx}}\right)$:

$$\widehat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\left\{\mathrm{N}\cdot\left(\frac{1}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{1}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\} = -\frac{\hbar^2}{2\mathrm{m}}\frac{\partial}{\partial \mathrm{x}}\left\{\mathrm{N}\cdot\left(\frac{\mathrm{ik}}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{-\mathrm{ik}}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\}$$

$$= -\frac{\hbar^2}{2\mathrm{m}}\left\{\mathrm{N}\cdot\left(\frac{-\mathrm{k}^2}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{-\mathrm{k}^2}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\}$$

The next step is to factor out $-\mathrm{k}^2$ which gives us:

$$\widehat{\mathrm{H}}\psi = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}\left\{\mathrm{N}\cdot\left(\frac{1}{2}\mathrm{e}^{\mathrm{ikx}} + \frac{1}{2}\mathrm{e}^{-\mathrm{ikx}}\right)\right\} = \mathrm{E}\psi$$

where again we see that $\mathrm{E} = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}$. So, everything seems fine, but why are we using this approach? While solving $\hat{\mathrm{H}}\psi$ using the complex representation of $\psi = \mathrm{N} \cdot \cos(\mathrm{kx})$ 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 $\psi = \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}$. In this case, which do you think is harder to solve:

$$\hat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}} \frac{\partial^2}{\partial \mathrm{x}^2} \left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\}$$

or:

$$\hat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}} \frac{\partial^2}{\partial \mathrm{x}^2} \{\mathrm{N} \cdot \cos(\mathrm{kx}) + \mathrm{i} \cdot \sin(\mathrm{kx})\}$$

Just for the heck of it let's solve the former:

$$\hat{\mathrm{H}}\psi = -\frac{\hbar^2}{2\mathrm{m}} \frac{\partial^2}{\partial \mathrm{x}^2} \left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\} = -\frac{\hbar^2}{2\mathrm{m}} \frac{\partial}{\partial \mathrm{x}} \left\{\mathrm{ik} \cdot \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\} = -\frac{\hbar^2}{2\mathrm{m}} \left\{\mathrm{i}^2 \mathrm{k}^2 \cdot \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\} = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}} \left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\}$$

Taking the derivative of an exponential is easy, and just like the previous example, we see that $\mathrm{E} = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}$. This wasn't nearly as hard as taking the double derivative of two trig functions!

12.4.2.1 Applications of other operators. Let's continue to work with $\psi = \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}$, from which we will extract the momentum via $\hat{\mathrm{p}}$:

$$\hat{\mathrm{p}}\psi = \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathrm{x}} \left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\} = \frac{\hbar}{\mathrm{i}} \left\{\mathrm{ik} \cdot \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\} = \hbar\mathrm{k}\left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\}$$

Here we get a "pass" on the eigenvalue equation $\hat{\Omega}\Phi = \omega \cdot \Phi$ 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 $\mathrm{p} = \hbar\mathrm{k}$ and it has an energy of $\mathrm{E} = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}$. Notice the consistency, as in the absence of potential the total energy is $\mathrm{E} = \frac{\mathrm{p}^2}{2\mathrm{m}}$, and inserting p= $\hbar\mathrm{k}$ yields $\mathrm{E} = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}$. If the wavefunction of the electron was $\psi = \mathrm{N} \cdot \mathrm{e}^{-\mathrm{ikx}}$, we would have still found $\frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}$ of energy but $-\hbar\mathrm{k}$ of momentum (note that this is still consistent with $\mathrm{E} = \frac{\mathrm{p}^2}{2\mathrm{m}}$). Why would one wavefunction have a positive momentum and the other negative? Why, the interpretation is simple, $\psi = \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}$ represents a particle moving forward and $\psi = \mathrm{N} \cdot \mathrm{e}^{-\mathrm{ikx}}$ is moving backwards!

Now let's double check our math abilities one last time with $\psi = \mathrm{N} \cdot \cos(\mathrm{kx})$, from which we will calculate the momentum.

$$\hat{\mathrm{p}}\psi = \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathrm{x}} \{\mathrm{N} \cdot \cos(\mathrm{kx})\} = \frac{-\hbar\mathrm{k}}{\mathrm{i}} \{\mathrm{N} \cdot \sin(\mathrm{kx})\} = \mathrm{i}\hbar\mathrm{k}\{\mathrm{N} \cdot \sin(\mathrm{kx})\}$$

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:

$$\hat{p}\{N \cdot \cos(kx)\} \neq \hat{p}\{N \cdot \sin(kx)\}$$

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 $\widehat{H}\psi = E\psi$. 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:

$$\psi = N \cdot \cos(kx) = \frac{N}{2}e^{ikx} + \frac{N}{2}e^{-ikx}$$

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 $\widehat{\Omega}$:

$$\langle\widehat{\Omega}\rangle = \int_{\text{lower limit}}^{\text{upper limit}} \psi^* \widehat{\Omega}\, \psi \cdot \partial\tau$$

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 $\psi = N \cdot \cos(kx)$:

$$\langle \hat{p} \rangle = \int_{\text{lower limit}}^{\text{upper limit}} \{\mathrm{N} \cdot \cos(\mathrm{kx})\}^* \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathrm{x}} \{\mathrm{N} \cdot \cos(\mathrm{kx})\} \cdot \partial \mathrm{x}$$

$$\frac{-\hbar}{\mathrm{i}} \mathrm{N}^2 \int_{-\infty}^{\infty} \cos(\mathrm{kx}) \cdot \sin(\mathrm{kx}) \cdot \partial \mathrm{x}$$

When we look up this integral off the internet, we find $\int_{-\infty}^{\infty} \cos(\mathrm{kx}) \cdot \sin(\mathrm{kx}) \cdot \partial \mathrm{x} = 0$. 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” $\Phi = \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}$ eigenfunction of momentum, that being the:

$$\langle \hat{p} \rangle = \int_{\text{lower limit}}^{\text{upper limit}} \left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\}^* \frac{\hbar}{\mathrm{i}} \frac{\partial}{\partial \mathrm{x}} \left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\} \cdot \partial \mathrm{x} =$$

$$\langle \hat{p} \rangle = \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \mathrm{N}^* \cdot \mathrm{e}^{-\mathrm{ikx}} \cdot \mathrm{ik} \cdot \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}} \cdot \partial \mathrm{x} =$$

$$\langle \hat{p} \rangle = \frac{\hbar \mathrm{ik}}{\mathrm{i}} \int_{-\infty}^{\infty} \mathrm{N}^* \cdot \mathrm{e}^{-\mathrm{ikx}} \cdot \mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}} \cdot \partial \mathrm{x} = \hbar \mathrm{k} \int_{-\infty}^{\infty} \Phi^* \Phi \cdot \partial \mathrm{x} = \hbar \mathrm{k}$$

where the complex conjugate $\left\{\mathrm{N} \cdot \mathrm{e}^{\mathrm{ikx}}\right\}^*$ is: $\mathrm{N}^* \cdot \mathrm{e}^{-\mathrm{ikx}}$, and we used the formula $\int \Phi^* \Phi \, \partial \mathrm{x} = \int |\Phi|^2 \, \partial \mathrm{x} = 1$ in the last step which is the definition of normalization. While we determined the corrent momentum, you might ask, why not stick with $\hat{\Omega} \Phi = \omega \cdot \Phi$ 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 $\hat{\Omega}$, the answer is seen in a simple derivation:

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} \Phi^*\hat{\Omega}\Phi \cdot \partial\tau = \int_{-\infty}^{\infty} \Phi^* \cdot \omega \cdot \Phi \cdot \partial\tau = \omega \cdot \int_{-\infty}^{\infty} \Phi^* \cdot \Phi \cdot \partial\tau = \omega$$

where we assume that Φ is normalized. However, this proof breaks down when we are not applying an eigenfunction of the operator, i.e. when $\hat{\Omega}\psi \neq \omega \cdot \psi$. 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 $\hat{\Omega}$ has two eigenfunctions Φ_1 and Φ_2, but ψ is not an eigenfunction of $\hat{\Omega}$. Upon further analysis you realize that ψ is a linear combination of the Φ's:

$$\psi = c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2$$

where c_1 and c_2 are constants. When you apply the above to the expectation value expression:

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} \psi^*\hat{\Omega}\psi \cdot \partial\tau = \int_{-\infty}^{\infty} \{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\}^*\hat{\Omega}\{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\} \cdot \partial\tau$$

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:

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} \{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\}^*\hat{\Omega}\{c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2\} \cdot \partial\tau$$

$$= \int_{-\infty}^{\infty} \left\{c_1^*\Phi_1^*\hat{\Omega}c_1\Phi_1 + c_2^*\Phi_2^*\hat{\Omega}c_2\Phi_2 + c_1^*\Phi_1^*\hat{\Omega}c_2\Phi_2 + c_2^*\Phi_2^*\hat{\Omega}c_1\Phi_1\right\} \cdot \partial\tau$$

This can be broken up into four smaller integrals which is less scary.

$$\langle\hat{\Omega}\rangle = \int_{-\infty}^{\infty} c_1^*\Phi_1^*\hat{\Omega}c_1\Phi_1 \cdot \partial\tau + \int_{-\infty}^{\infty} c_2^*\Phi_2^*\hat{\Omega}c_2\Phi_2 \cdot \partial\tau + \int_{-\infty}^{\infty} c_1^*\Phi_1^*\hat{\Omega}c_2\Phi_2 \cdot \partial\tau + \int_{-\infty}^{\infty} c_2^*\Phi_2^*\hat{\Omega}c_1\Phi_1 \cdot \partial\tau$$

We can simplify this further using the relationships:

$$\hat{\Omega}c_1\Phi_1 = \omega_1 \cdot c_1\Phi_1, \qquad \hat{\Omega}c_2\Phi_2 = \omega_2 \cdot c_2\Phi_2, \qquad c_1^*c_1 = |c_1|^2, \qquad \text{and } c_2^*c_2 = |c_2|^2$$

to yield:

$$\langle\hat{\Omega}\rangle = |c_1|^2 \cdot \omega_1 \cdot \int_{-\infty}^{\infty} |\Phi_1|^2 \cdot \partial\tau + |c_2|^2 \cdot \omega_2 \cdot \int_{-\infty}^{\infty} |\Phi_2|^2 \cdot \partial\tau + c_1^*c_2 \cdot \omega_2 \int_{-\infty}^{\infty} \Phi_1^*\Phi_2 \cdot \partial\tau + c_2^*c_1 \cdot \omega_1 \int_{-\infty}^{\infty} \Phi_2^*\Phi_1 \cdot \partial\tau$$

Now the above monster can be solved using something that we know already, which is that eigenfunctions are normalized:

$$\int_{-\infty}^{\infty} |\Phi_1|^2 \cdot \partial\tau = \int_{-\infty}^{\infty} |\Phi_2|^2 \cdot \partial\tau = 1$$

Now we also must introduce a new concept called "orthonormality" for the 3rd and 4th expression above:

$$\int_{-\infty}^{\infty} \Phi_1^*\Phi_2 \cdot \partial\tau = \int_{-\infty}^{\infty} \Phi_2^*\Phi_1 \cdot \partial\tau = 0$$

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:

$$\langle\hat{\Omega}\rangle = |c_1|^2 \cdot \omega_1 + |c_2|^2 \cdot \omega_2$$

Now you may have said to yourself, "I can't imagine when would I every run into an equation like: $\psi = c_1 \cdot \Phi_1 + c_2 \cdot \Phi_2$." Actually, you already have, with:

$$N \cdot \cos(kx) = \frac{N}{2}e^{ikx} + \frac{N}{2}e^{-ikx}$$

Here, $\psi = N \cdot \cos(kx)$, $c_1 = \frac{1}{2}$ and $c_2 = \frac{1}{2}$ and $\Phi_1 = e^{ikx}$ and $\Phi_2 = e^{-ikx}$. We have already shown that ψ is not the eigenfunction of the momentum operator $\hat{p}$, although Φ_1 and Φ_2 are since $\hat{p}\Phi_1 = \hbar k \cdot \Phi_1$ and $\hat{p}\Phi_2 = -\hbar k \cdot \Phi_2$. 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:

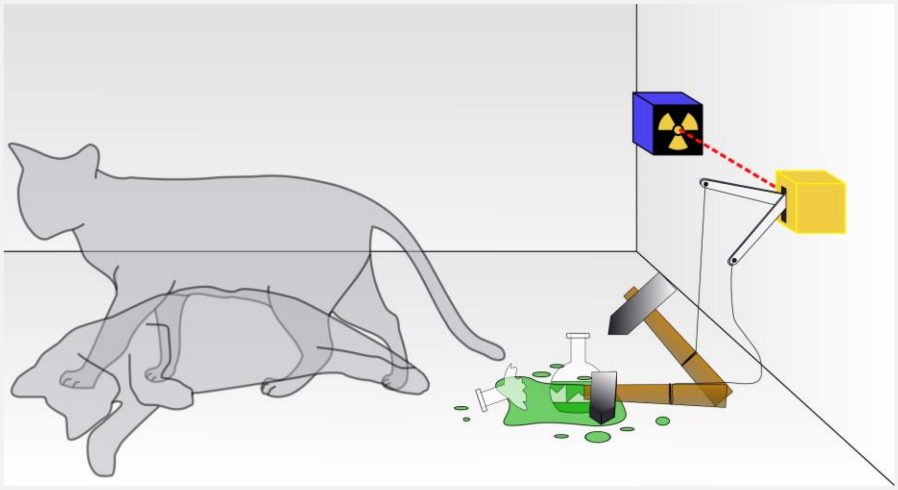
$$\langle\hat{p}\rangle = \left|\frac{1}{2}\right|^2 \cdot \hbar k + \left|\frac{1}{2}\right|^2 \cdot (-\hbar k) = 0$$

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 $\psi = N \cdot \cos(kx)$ describes a particle that isn't moving. $\psi = N \cdot \sin(kx)$ would do the same thing.

12.4.3 Schrodinger's Cat. In the previous example, it was found that a quantum particle described by the wavefunction $\psi = N \cdot \cos(kx)$ or $\psi = N \cdot \sin(kx)$ 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

Schrödinger's Cat

The famous Schrödinger's cat is a feline placed in a death trap. Specifically, a box with a radioactive element, and once a Geiger counter reads off some radiation upon which a vial of poison opens and the cat dies. Since you can't know if that event has happened, the cat must be simultaneously alive and dead, and if you try to cheat and look then the trap sets and the cat is definitely dead. The idea behind this thought experiment was to expose quantum mechanics as ridiculous; however, it is the interpretation that is non-sensical here. What is being said isn't that the cat is a zombie-like state, rather, that you as an exterior observer simply don't know that cat's status. And as a result, you have to use a description (i.e. wavefunction) whereby the cat is both alive and dead. However, the cat is most definitely one or the other, you just don't know which one it is.



have a conundrum because we already demonstrated that $E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$! 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 Schrodinger'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 $\psi = N \cdot \cos(kx)$, and recall for the eigenvalue equation to work properly (for ψ to be an eigenfunction of $\widehat{\Omega}$) we need to see that $\widehat{\Omega}\psi = \omega \cdot \psi$:

$$\hat{x}\psi = x \cdot N \cdot \cos(kx)$$

Whups- this is a fail, the wavefunction on the right is supposed to be a number (ω) multiplying the original wavefunction. However, if $f(x) = \cos(kx)$ and $g(x) = x \cdot \cos(kx)$, then clearly $f(x) \neq g(x)$ since "x" is not a finite value like 5 or π. 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 $\psi = N \cdot \cos(kx)$, 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 $\widehat{\Omega}$, then the following is true:

$$\int_{\text{lower limit}}^{\text{upper limit}} \psi_{n'}^{*}\psi_n \cdot \partial\tau = \delta_{n',n}$$

Where d is the Kronecker delta function:

$$\delta_{n',n} = \{^{1,\text{if } n'=n}_{0,\text{if } n'\neq n}$$

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:

$$\int \psi_{n'}^{*}\widehat{\Omega}\psi_{n} \cdot \partial\tau = \int \psi_{n}\left(\widehat{\Omega}\psi_{n'}\right)^{*} \cdot \partial\tau$$

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 $\widehat{\Omega}\psi_n = \omega_n\psi_n$. 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:

$$\int \psi_{n'}^{*}\widehat{\Omega}\psi_{n} \cdot \partial\tau = \int \psi_{n'}^{*}\omega_n\psi_{n} \cdot \partial\tau = \omega_n \cdot \int \psi_{n'}^{*}\psi_{n} \cdot \partial\tau$$

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 $\int \psi_{n'}^{*}\widehat{\Omega}\psi_{n} \cdot \partial\tau = \int \psi_{n}\left(\widehat{\Omega}\psi_{n'}\right)^{*} \cdot \partial\tau$ then:

$$\left(\omega_n - \omega_{n'}^{*}\right)\int \psi_{n'}^{*}\psi_{n} \cdot \partial\tau = 0$$

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:

$$\int \psi^*_{n'}\psi_n \cdot \partial\tau = \{^{1,\text{if } n'=n}_{0,\text{if } n'\neq n}$$

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: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ 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 $\psi = N \cdot \cos(kx)$ and $\psi = N \cdot \sin(kx)$ 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 $\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$. 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 $\psi(x)$ has to be $\psi(0) = 0$ at x=0, and $\psi(L) = 0$ 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 $\sin(x = L) = 0$. A sine wave always starts at 0, and it next crosses 0 at π. Thus, we know that:

$$\psi(x) = N \cdot \sin\left(\pi\frac{x}{L}\right)$$

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 $\psi(x) = N \cdot \sin\left(2\pi \frac{x}{L}\right)$. And we can keep figuring out new solutions until we see that there is a general relationship

$\psi_n(x) = N \cdot \sin\left(n\pi \frac{x}{L}\right)$, 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:

$$\int \sin^2(ax) \, \partial x = \frac{x}{2} - \frac{1}{4a} \sin\,(2ax)$$

and thus: $\int \sin^2\left(n\pi \frac{x}{L}\right) \partial x = \frac{x}{2} - \frac{L}{4n\pi} \sin\,(2n\pi \frac{x}{L})$. When placed into a definite integral:

$$\int_0^L \sin^2\left(n\pi \frac{x}{L}\right) \cdot \partial x = \frac{x}{2} - \frac{L}{4n\pi} \sin\,(2n\pi \frac{x}{L})\bigg]_{x=0}^{x=L} = \frac{L}{2} - \frac{L}{4n\pi} \sin(2n\pi) = \frac{L}{2}$$

because $\sin(2n\pi) = 0$ since n is a whole number integer, i.e. since n=1, 2, 3… then $\sin(2n\pi) = \sin(4\pi) = \sin(6\pi) = 0$.

As a result, the proper normalized particle in a box wavefunctions are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(n\pi \frac{x}{L}\right)$$

Now for their interpretation, first we can calculate the energy. We will use the eigenvalue expression $\widehat{H}\psi_n(x) = E \cdot \psi_n(x)$ since this is usually the fastest way if you know you are dealing with the eigenfunctions of the operator (here, the Hamiltonian).

$$\widehat{H}\psi_n(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_n(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \sqrt{\frac{2}{L}} \cdot \sin\left(n\pi \frac{x}{L}\right) = \frac{n^2\pi^2}{2mL^2} \sqrt{\frac{2}{L}} \cdot \sin\left(n\pi \frac{x}{L}\right)$$

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.

$$\langle\hat{x}\rangle = \int_{\text{lower}}^{\text{upper}} \psi_{n'}^{*}\hat{x}\psi_n \cdot \partial\tau = \int_0^L \left(\sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right)\right)^{*} \cdot x \cdot \sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right) \cdot \partial x$$

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:

$$\langle\hat{x}\rangle = \frac{2}{L}\int_0^L x \cdot \sin^2\left(n\pi\frac{x}{L}\right) \cdot \partial x$$

Use of a table of trigonometric identities yields:

$$\langle\hat{x}\rangle = \frac{2}{L}\int x \cdot \sin^2\left(n\pi\frac{x}{L}\right) \cdot \partial x = \frac{2}{L}\left\{\frac{x^2}{2} - \frac{xL}{4n\pi}\sin\left(2n\pi\frac{x}{L}\right) - \frac{x^2}{4} - \frac{L^2}{8n^2\pi^2}\cos\left(2n\pi\frac{x}{L}\right)\right]_{x=0}^{x=L}\right\}$$

Inputting the limits and using the normalizer gives:

$$\langle\hat{x}\rangle = L - \frac{L}{2n\pi}\sin(2n\pi) - \frac{L}{2} - \frac{L}{4n^2\pi^2}\cos(2n\pi) + \frac{L}{4n^2\pi^2}$$

Since $\sin(2n\pi)$ and $\cos(2n\pi)$ 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:

$$\langle\hat{p}\rangle = \int_{\text{lower}}^{\text{upper}} \psi_{n'}^{*}\hat{x}\psi_n \cdot \partial\tau = \int_0^L \left(\sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right)\right)^{*} \cdot \frac{\hbar}{i}\frac{\partial}{\partial x}\sqrt{\frac{2}{L}} \cdot \sin\left(n\pi\frac{x}{L}\right) \cdot \partial x$$

Several steps of simplification yield:

$$\langle\hat{p}\rangle = \int_{\text{lower}}^{\text{upper}} \psi_{n'}^{*}\hat{x}\psi_n \cdot \partial\tau = \frac{2}{L}\frac{\hbar}{i}\frac{n\pi}{L}\int_0^L \cdot \sin\left(n\pi\frac{x}{L}\right) \cdot \cos\left(n\pi\frac{x}{L}\right) \cdot \partial x$$

Since $\int \sin(ax) \cdot \cos(ax)\,\partial x = -\frac{1}{4a}\cos(2ax)$ we find that:

$$\langle\hat{p}\rangle = \frac{2\hbar n\pi}{iL^2}\left\{-\frac{L}{4n\pi}\cos\left(2n\pi\frac{x}{L}\right)\right\}\Bigg]_{x=0}^{x=L} = -\frac{\hbar}{2iL}\cos(2n\pi) + \frac{\hbar}{2iL}$$

And since $\cos(2n\pi) = 0$ 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.

Problems: Numerical

1. More on eigenvectors. A particle with some kinetic energy is created in an empty, infinite universe. You are 60% certain it is moving to the right (momentum= $+\hbar k$) and thus there is a 40% chance it is moving left (momentum= $-\hbar k$). If I write the wavefunction $\Psi(x)$ as a linear sum of normalized momentum eigenvectors: $N \cdot \Phi_n(x)$, where N is the normalization constant, the result is:

$$\Psi(x) = c_1 N\Phi_1(x) + c_2 N\Phi_2(x) = 0.7746 \cdot N \cdot e^{ikx} + 0.6325 \cdot N \cdot e^{-ikx}$$

a. How did I determine that c_1=0.7746 and c_2=0.6325? Does it have anything to do with the functions that they multiply (i.e $N \cdot e^{ikx}, N \cdot e^{-ikx}$)? (hint: square the numbers) **(2 pts)**

b. Please derive the expectation value $\langle p \rangle$ of momentum for this particle using the formula:

$$\langle p \rangle = \int_{-\infty}^{\infty} [c_1\Phi_1(x) + c_2\Phi_2(x)]^* \frac{\hbar}{i}\frac{\partial}{\partial x}[c_1\Phi_1(x) + c_2\Phi_2(x)]\,\partial x$$

Hint: $\int_{-\infty}^{\infty} N^2 e^{-ikx} e^{ikx} \cdot \partial x = 1$, $\int_{-\infty}^{\infty} N^2 e^{ikx} e^{ikx} \cdot \partial x = 0$ and $\int_{-\infty}^{\infty} N^2 e^{-ikx} e^{-ikx} \cdot \partial x = 0$ **(10 pts)**

2. More on eigenvectors. A particle with some kinetic energy is created in an empty, infinite universe. You are 75% certain it is moving to the right (momentum $=\hbar k$) and thus there is a 25% chance it is moving left (momentum= $-\hbar k$). If I write the wavefunction $\Psi(x)$ as a linear sum of normalized momentum eigenvectors: $N \cdot \Phi_n(x)$, where N is the normalization constant, the result is:

$$\Psi(x) = c_1 N\Phi_1(x) + c_2 N\Phi_2(x) = 0.866 \cdot N \cdot e^{ikx} + 0.500 \cdot N \cdot e^{-ikx}$$

a. How did I determine that c_1=0.866 and c_2=0.500? Does it have anything to do with the functions that they multiply (i.e $N \cdot e^{ikx}, N \cdot e^{-ikx}$)? (hint: square the numbers) **(2 pts)**

b. Please derive the expectation value $\langle p \rangle$ of momentum for this particle using the formula:

$$\langle p \rangle = \int_{-\infty}^{\infty} [c_1\Phi_1(x) + c_2\Phi_2(x)]^* \frac{\hbar}{i}\frac{\partial}{\partial x}[c_1\Phi_1(x) + c_2\Phi_2(x)]\,\partial x$$

Hint: $\int_{-\infty}^{\infty} N^2 e^{-ikx} e^{ikx} \cdot \partial x = 1$, $\int_{-\infty}^{\infty} N^2 e^{ikx} e^{ikx} \cdot \partial x = 0$ and $\int_{-\infty}^{\infty} N^2 e^{-ikx} e^{-ikx} \cdot \partial x = 0$ **(10 pts)**

Problems: Theoretical or Explain in Words

1. Math practice! Operate on $\Psi = r \cdot \sin(\theta)$ using the operator: **(10 pts)**

$$\left(\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\cos(\theta)\frac{\partial}{\partial r}r\right) - 2\frac{\cos^2(\theta)}{\sin^2(\theta)}$$

Hint: $\frac{\partial}{\partial\theta}\{\cos(\theta) \cdot \sin(\theta)\} = \cos^2(\theta) - \sin^2(\theta)$, and Ψ is an eigenfunction with an eigenvalue of -2.

2. Math practice! Operate on $\Psi = r \cdot \sin(\theta)$ using the operator:

$$\left(\frac{\partial}{\partial\theta}\tan(\theta)\frac{\partial}{\partial r}r\right) - 2\frac{\tan(\theta)\sec(\theta)}{\sin(\theta)}$$

Hint: $\frac{\partial}{\partial\theta}\{\tan(\theta) \cdot \sin(\theta)\} = \sin(\theta) + \tan(\theta)\sec(\theta)$, and Ψ is an eigenfunction with an eigenvalue of 2. **(10 pts)**

3. If I have a particle that does not experience any sort of potential energy (all energy is kinetic), then the Schrodinger equation is:

$$\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2\Psi(\mathrm{x})}{\partial\mathrm{x}^2} = \mathrm{E}\cdot\Psi(\mathrm{x})$$

which simplifies to:

$$\frac{\partial^2\Psi(\mathrm{x})}{\partial\mathrm{x}^2} = -\mathrm{k}^2\cdot\Psi(\mathrm{x})$$

where $\mathrm{k}^2 = \left[\frac{2\mathrm{m}\cdot\mathrm{E}}{\hbar^2}\right]$. Solutions include $\Psi(\mathrm{x}) = \mathrm{e}^{\mathrm{ik}\cdot\mathrm{x}}$ and $\Psi(\mathrm{x}) = \mathrm{e}^{-\mathrm{ik}\cdot\mathrm{x}}$, both of which have an energy of: $\mathrm{E} = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}$.

a. Please show that a linear combination of $\mathrm{e}^{\mathrm{ik}\cdot\mathrm{x}}$ and $\mathrm{e}^{-\mathrm{ik}\cdot\mathrm{x}}$, i.e. $\Psi(\mathrm{x}) = \mathrm{e}^{\mathrm{ik}\cdot\mathrm{x}} + \mathrm{e}^{-\mathrm{ik}\cdot\mathrm{x}}$, is also eigenfunction of the Hamiltonian with the same energy $\mathrm{E} = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}$. **(5 pts)**

b. Please show that the wavefunction: $\Psi(\mathrm{x}) = \mathrm{e}^{\mathrm{ik}\cdot\mathrm{x}} - \mathrm{e}^{-\mathrm{ik}\cdot\mathrm{x}}$ is also an eigenfunction of the Hamiltonian with energy $\mathrm{E} = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}$. **(5 pts)**

4. The eigenfunction of an operator $\Phi(\mathrm{x})$, such as $\hat{\mathrm{p}}_{\mathrm{x}} = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\mathrm{x}}$, has the following property:

$$\hat{\mathrm{p}}_{\mathrm{x}}\Phi(\mathrm{x}) = \omega\cdot\Phi(\mathrm{x})$$

where ω is just some constant(s). Which of the following functions are eigenfunctions of the momentum operator?

a. $\mathrm{k}\cdot\mathrm{x}^2$ **b.** $\mathrm{e}^{\mathrm{k}\cdot\mathrm{x}^2}$ **c.** $\cos(\mathrm{k}\cdot\mathrm{x})$ **d.** $\mathrm{e}^{\mathrm{ikx}}$ **e.** $\mathrm{e}^{\mathrm{ikx}} + \mathrm{e}^{-\mathrm{ikx}}$ **(5 pts)**

5. The eigenfunction of an operator $\Phi(\mathrm{x})$, such as $\hat{\mathrm{p}}_{\mathrm{x}} = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial\mathrm{x}}$, has the following property:

$$\hat{\mathrm{p}}_{\mathrm{x}}\Phi(\mathrm{x}) = \omega\cdot\Phi(\mathrm{x})$$

where ω is just some constant(s). Which of the following functions are eigenfunctions of the momentum operator?

a. $\mathrm{k}\cdot\mathrm{x}^2$ **b.** $\mathrm{e}^{\mathrm{k}\cdot\mathrm{x}^2}$ **c.** $\sin(\mathrm{k}\cdot\mathrm{x})$ **d.** $\mathrm{e}^{\mathrm{ikx}}$ **e.** $\mathrm{e}^{\mathrm{ikx}} - \mathrm{e}^{-\mathrm{ikx}}$ **(5 pts)**

6. Which of the following are eigenfunctions of the kinetic energy operator $\frac{\hat{\mathrm{p}}_{\mathrm{x}}^2}{2\mathrm{m}} = \frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial\mathrm{x}^2}$?

a. $\mathrm{k}\cdot\mathrm{x}$ **b.** $\mathrm{k}\cdot\mathrm{x}^2$ **c.** $\mathrm{e}^{\mathrm{k}\cdot\mathrm{x}^2}$ **d.** $\cos(\mathrm{k}\cdot\mathrm{x})$ **(8 pts)**

e. Given the Schrodinger equation: $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2\Psi(\mathrm{x})}{\partial\mathrm{x}^2} = \mathrm{E}\cdot\Psi(\mathrm{x})$, and assume that we know that the energy is 0. In this case, is it acceptable for the wavefunction to be Y(x)=k·x? **(5 pts)**

7. The "flux" operator: $\Psi^*\frac{\partial\Psi}{\partial\mathrm{x}} - \Psi\frac{\partial\Psi^*}{\partial\mathrm{x}}$ tells you whether a wavefunction is moving left or right. If the answer is + or - , the wavefunction is moving either right or left. If you get 0, then the wavefunction is not moving.

Can you apply the flux operator on the following:

a. $\psi = \mathrm{e}^{-\mathrm{ikx}}$ **b.** $\psi = \sin(\mathrm{k}\cdot\mathrm{x})$ **c.** $\psi = \mathrm{e}^{-\mathrm{kx}^2}$ **(9 pts)**

and tell me whether the wavefunction is moving left, right, or isn't moving.

8. The "flux" operator: $\Psi^*\frac{\partial\Psi}{\partial\mathrm{x}} - \Psi\frac{\partial\Psi^*}{\partial\mathrm{x}}$ tells you whether a wavefunction is moving left or right. If the answer is + or - , the wavefunction is moving either right or left. If you apply the operator and get 0, then the wavefunction is not moving.

Can you apply the flux operator on the following:

a. $\psi = \mathrm{e}^{\mathrm{ikx}}$ **b.** $\psi = \cos(\mathrm{k}\cdot\mathrm{x})$ **c.** $\psi = \mathrm{e}^{-\mathrm{kx}^2}$ **(9 pts)**

and tell me whether the wavefunction is moving left, right, or isn't moving.

9. Please normalize the wavefunction:

$$\Psi(\mathrm{x}) = \sqrt{\mathrm{x}} \cdot \sin\left(\frac{\pi}{\mathrm{L}}\mathrm{x}\right)$$

For this problem you will need to use the on-line definite integral calculator:

https://www.wolframalpha.com/widgets/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605

Hint: Hopefully you know that the normalization is: $N = \frac{1}{\sqrt{\int_0^{\mathrm{L}} \Psi^{*} \cdot \Psi \cdot \partial \mathrm{x}}}$ **(5 pts)**

10. Charles Hermite showed that wavefunctions have the property:

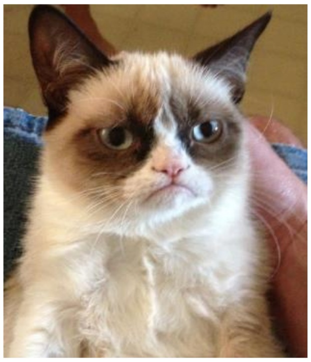
$$\int_{-\infty}^{\infty} \Psi_{\mathrm{j}}^{*}\Psi_{\mathrm{i}} \cdot \partial \mathrm{x} = 0$$

for all i≠j; this is called orthonormality. All the operators we study are Hermitian. For a particle in a box, the ground state is: $\sqrt{\frac{2}{\mathrm{L}}} \cdot \sin\left(\frac{\pi \mathrm{x}}{\mathrm{L}}\right)$ and all excited states are: $\sqrt{\frac{2}{\mathrm{L}}} \cdot \sin\left(\frac{\mathrm{n}\pi \mathrm{x}}{\mathrm{L}}\right)$ where n=2, 3, 4… Can you prove that $\int_0^{\mathrm{L}} \Psi_{\mathrm{j}}^{*}\Psi_{\mathrm{i}} \cdot \partial \mathrm{x} = 0$ where Ψ_{i} is the ground state and Ψ_{j} are the excited states? You should use an on-line integrator to show that $\int_0^{\mathrm{L}} \Psi_{\mathrm{j}}^{*}\Psi_{\mathrm{i}} \cdot \partial \mathrm{x}$ yields an expression that has "n" in it that is always 0 if n>1.

(5 pts)

Hint: The Wolfram web site often "hangs" on such calculations. To get it unstuck, hit the "=" on the lower right.

Top: Charles Hermite.
Bottom: Charles Hermite's cat.



Chapter 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:

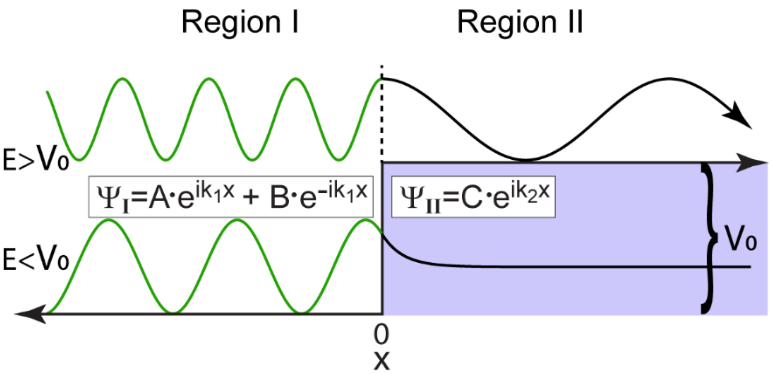


Figure 13.1. The step potential problem demonstrates how a quantum object reflects off a barrier.

$$\text{x} < 0 \text{ (left)}: \qquad \frac{-\hbar^2}{2\text{m}}\frac{\partial^2}{\partial \text{x}^2}\psi_{\text{I}}(\text{x}) = \text{E} \cdot \psi_{\text{I}}(\text{x})$$

$$\text{x} > 0 \text{ (right)}: \quad \frac{-\hbar^2}{2\text{m}}\frac{\partial^2}{\partial \text{x}^2}\psi_{\text{II}}(\text{x}) + \text{V}_0 \cdot \psi_{\text{II}}(\text{x}) = \text{E} \cdot \psi_{\text{II}}(\text{x})$$

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":

$$\psi_{\text{I}} = \text{A} \cdot \text{e}^{\text{i}\text{k}_1\text{x}} + \text{B} \cdot \text{e}^{-\text{i}\text{k}_1\text{x}}$$

The wavevector k_1 can be found by rearranging the Schrödinger equation: $\frac{\partial^2}{\partial \text{x}^2}\psi_{\text{I}}(\text{x}) = \frac{2\text{mE}}{\hbar^2} \cdot \psi_{\text{I}}(\text{x})$, which makes $\text{k}_1 = \sqrt{\frac{2\text{mE}}{\hbar^2}}$. Now as for the 2nd region, we first rearrange the Hamiltonian as:

$$\text{x} > 0 \text{ (right)}: \quad \frac{-\hbar^2}{2\text{m}}\frac{\partial^2}{\partial \text{x}^2}\psi_{\text{II}}(\text{x}) = (\text{E} - \text{V}_0) \cdot \psi_{\text{II}}(\text{x})$$

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:

$$\psi_{\text{II}} = \text{C} \cdot \text{e}^{\text{i}\text{k}_2\text{x}} + \text{D} \cdot \text{e}^{-\text{i}\text{k}_2\text{x}}$$

The wavevector k_2 can be found by simply replacing "E" in k_1 with $(\text{E} - \text{V}_0)$: $\text{k}_2 = \sqrt{\frac{2\text{m}(\text{E}-\text{V}_0)}{\hbar^2}}$. It is apparent that $k_2 < k_1$, 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:

$$\psi_{\mathrm{I}}(\mathrm{x}) = \mathrm{A} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_1\mathrm{x}}$$

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:

$$\psi_{\mathrm{I}}(\mathrm{x}) = \mathrm{A} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_1\mathrm{x}} + \mathrm{B} \cdot \mathrm{e}^{-\mathrm{i}\mathrm{k}_1\mathrm{x}}$$

If the particle transmits over the barrier it can only continue on to the right:

$$\psi_{\mathrm{II}}(\mathrm{x}) = \mathrm{C} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_2\mathrm{x}}$$

If you wonder why there is no leftward moving $\mathrm{e}^{-\mathrm{i}\mathrm{k}_2\mathrm{x}}$ “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 $\mathrm{A} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_1\mathrm{x}}$ as the incoming “A-wave”, $\mathrm{B} \cdot \mathrm{e}^{-\mathrm{i}\mathrm{k}_1\mathrm{x}}$ as the reflected “B-wave” and $\mathrm{C} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_2\mathrm{x}}$ as the transmitted “C-wave”. This is because the probability amplitude of the incoming wave is:

$$\left|\mathrm{A} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_1\mathrm{x}}\right|^2 = |\mathrm{A}|^2 \cdot \mathrm{e}^{-\mathrm{i}\mathrm{k}_1\mathrm{x}} \cdot \mathrm{e}^{\mathrm{i}\mathrm{k}_1\mathrm{x}} = |\mathrm{A}|^2 \cdot \mathrm{e}^0 = |\mathrm{A}|^2$$

The probability of reflecting is related to $|\mathrm{B}|^2$ and likewise the probability of transmission is related to $|\mathrm{C}|^2$.

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: $\mathrm{R} = \frac{|\mathrm{B}|^2}{|\mathrm{A}|^2}$ 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:

$$\psi_{\mathrm{I},(\mathrm{x}=0)} = \psi_{\mathrm{II},(\mathrm{x}=0)} \text{ (continuous) and: } \frac{\partial \psi_{\mathrm{I},(\mathrm{x}=0)}}{\partial x} = \frac{\partial \psi_{\mathrm{II},(\mathrm{x}=0)}}{\partial x} \text{ (smooth)}$$

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: $\psi_{\mathrm{I}}{}' = \psi_{\mathrm{II}}{}'$ by the continuous one: $\psi_{\mathrm{I}} = \psi_{\mathrm{II}}$ at the boundary:

$$\frac{\psi_{\mathrm{I}}{}'_{(x=0)}}{\psi_{\mathrm{I}(x=0)}} = \frac{\psi_{\mathrm{II}}{}'_{(x=0)}}{\psi_{\mathrm{II}(x=0)}}$$

(For those readers who are mathematically inclined, this is the log derivative $\partial \ln(\psi) = \frac{\psi'}{\psi}$)

When we insert the equations and make x=0 we are left with:

$$\frac{A \cdot ik_1 e^0 - B \cdot ik_1 e^0}{A \cdot e^0 + B \cdot e^0} = \frac{C \cdot ik_2 e^0}{C \cdot e^0}$$

Since $e^0 = 1$ and the C's on the right cancel:

$$k_1 A - k_1 B = k_2 A + k_2 B$$

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, $1\ \mathrm{eV} = 1.602 \times 10^{-19}$ 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:

$$\psi_{\mathrm{II}}(x) = C \cdot e^{i^2 \cdot k_2' x} = C \cdot e^{-k_2' x}$$

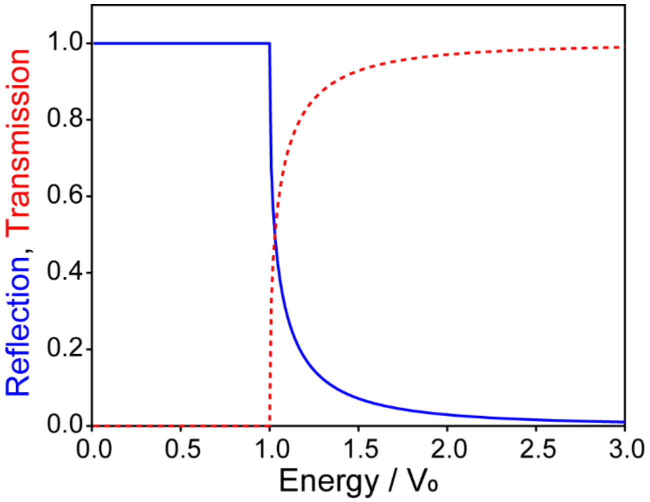


Figure 13.2. Reflection and transmission as a function of the particle's energy.

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, $\psi_{III}(x) = E \cdot e^{ik_1x}$, 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,

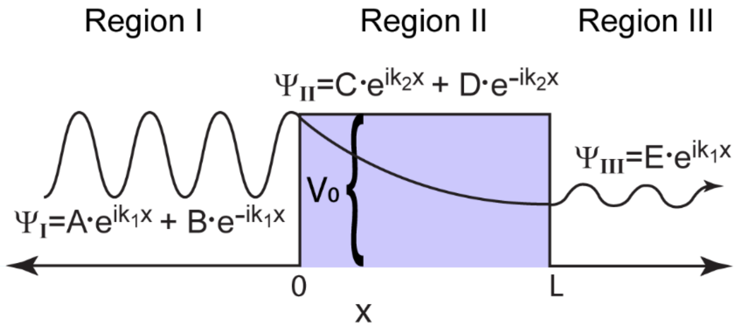


Figure 13.3. The finite barrier problem demonstrates the process of tunneling through a barrier.

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.

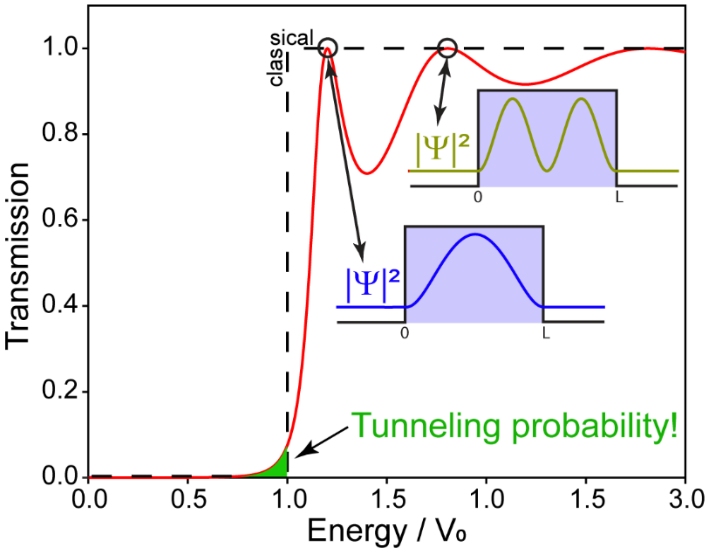


Figure 13.4. The transmission of a quantum particle reveals tunneling and resonant behavior. Inset shows that a wavefunction’s λ is the same as the length of the trap when on resonance.

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:

$$x < 0 \qquad V(x) = \infty$$

$$0 \leq x \leq L \quad V(x) = 0$$

$$x > L \qquad V(x) = \infty$$

This surface is shown in Figure 13.5. We seek a solution to the Schrodinger 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:

$$\psi_{II}(x) = A \cdot e^{ik \cdot x} + B \cdot e^{-ik \cdot x}$$

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:

$$\mathrm{A} \cdot \mathrm{e}^0 + \mathrm{B} \cdot \mathrm{e}^0 = 0$$

and as a result $\mathrm{B} = -\mathrm{A}$. This implies that the wavefunction is a sine wave as $\sin(\mathrm{k} \cdot \mathrm{x}) = \mathrm{A} \cdot \mathrm{e}^{\mathrm{ik \cdot x}} - \mathrm{A} \cdot \mathrm{e}^{-\mathrm{ik \cdot x}}$ if $\mathrm{A} = \frac{1}{2\mathrm{i}}$. Thus, the boundary condition reveals that:

$$\psi_{\mathrm{II}}(\mathrm{x}) = \sin(\mathrm{k} \cdot \mathrm{x})$$

Now we have to apply the second boundary condition at x=L:

$$\sin(\mathrm{k} \cdot \mathrm{L}) = 0$$

This can only be true if $\mathrm{k}_1\mathrm{L} = \mathrm{n}\pi$, allowing us to solve for the wave vector:

$$\mathrm{k} = \frac{\mathrm{n}\pi}{L}$$

where n is an integer that goes from 1,2,3… As a result, the wavefunction is:

$$\psi_{\mathrm{II}}(\mathrm{x}) = \mathrm{N} \cdot \sin\left(\frac{\mathrm{n}\pi}{\mathrm{L}}\mathrm{x}\right)$$

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:

$$\mathrm{N}^2 \int_0^{\mathrm{L}} \sin^2\left(\frac{\mathrm{n}\pi}{\mathrm{L}}\mathrm{x}\right) \partial \mathrm{x} = 1$$

which allows N to be defined as:

$$\mathrm{N} = \frac{1}{\sqrt{\int_0^{\mathrm{L}} \sin^2\left(\frac{\mathrm{n}\pi}{\mathrm{L}}\mathrm{x}\right) \partial \mathrm{x}}}$$

We solved the integral by looking it up on the internet: $\int_0^{\mathrm{L}} \sin^2\left(\frac{\mathrm{n}\pi}{\mathrm{L}}\mathrm{x}\right) \partial \mathrm{x} = \frac{L^2}{4}$, which means $\mathrm{N} = \sqrt{\frac{2}{\mathrm{L}}}$ and the full particle in a box wavefunction is: $\psi_{\mathrm{II}}(\mathrm{x}) = \sqrt{\frac{2}{\mathrm{L}}} \sin\left(\frac{\mathrm{n}\pi}{\mathrm{L}}\mathrm{x}\right)$. These wavefunctions are also orthogonal to each other: $\int \psi_{\upsilon'}^* \psi_{\upsilon}\, \partial \mathrm{x} = \delta_{\upsilon',\upsilon}$, 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 $\upsilon' \neq \upsilon$.

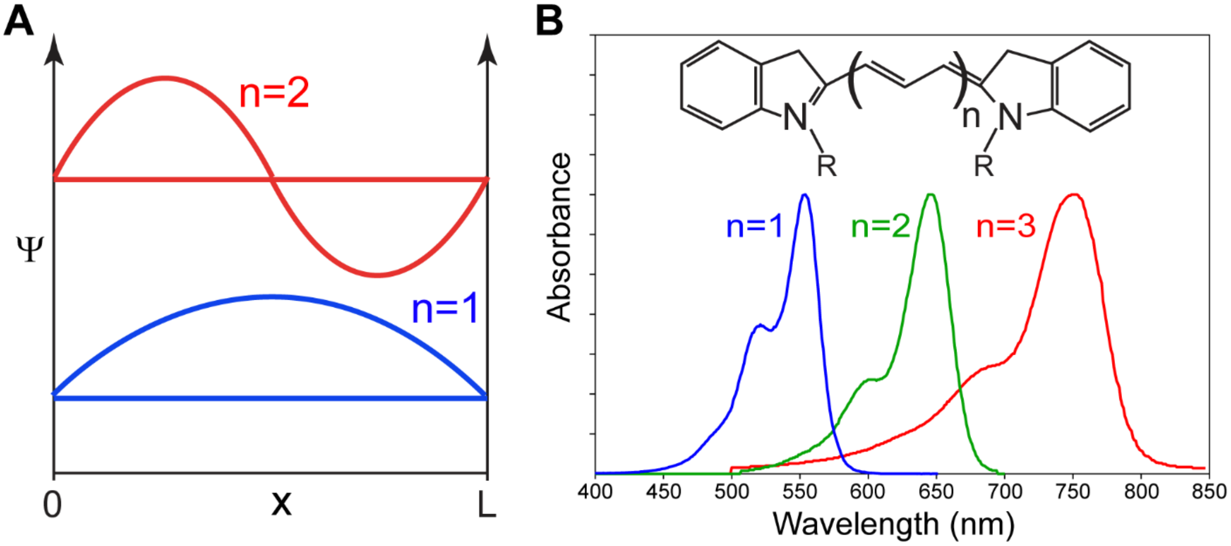


Figure 13.5 A. The particle in a box potential and first two states. **B.** The potential is a good model for cyanine dyes. As the number of conjugated bonds increases, the absorption energy drops to longer and longer wavelengths.

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 $\hat{H}\psi = E\psi$:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) = \frac{\hbar^2 n^2 \pi^2}{2mL^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right) = E \cdot \psi_{II}(x)$$

and thus:

$$E = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

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 1st 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 1st 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

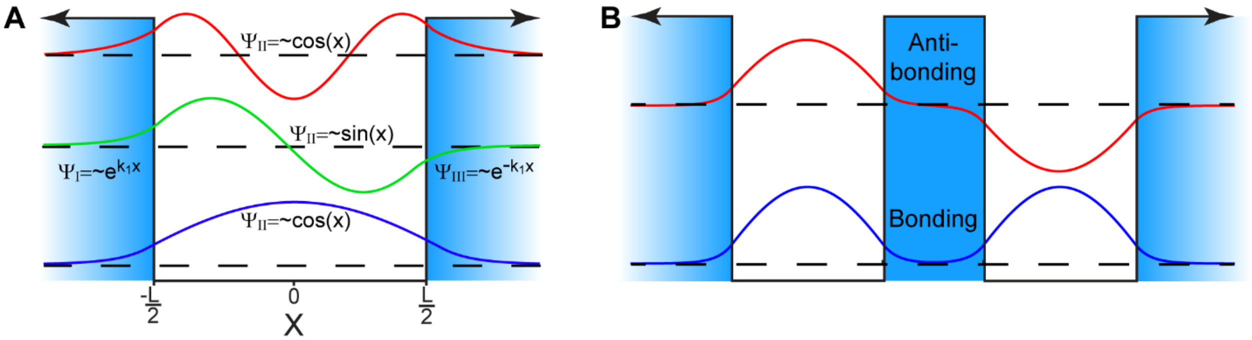


Figure 13.7A. The finite box problem is centered at x=0, and has alternating even- and odd-symmetric solutions. **B**. The ground and 1st excited state of a particle between two finite boxes look like bonding and antibonding orbitals.

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, $\psi_{II}(x) = B \cdot \cos(k_2 x)$, 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:

Figure 13.6. Semiconductor quantum dots change their emission color based on the size of the nanoparticle. Typical sizes are 2→10 nm.

$$A \cdot e^{-k_1 \cdot L/2} = B \cdot \cos\left(-k_2 \frac{L}{2}\right) \qquad \text{and} \qquad k_1 \cdot A \cdot e^{-k_1 \cdot L/2} = -k_2 \cdot B \cdot \sin\left(-k_2 \frac{L}{2}\right)$$

and likewise for region II/III:

$$B \cdot \cos\left(k_2 \frac{L}{2}\right) = C \cdot e^{-k_1 \cdot L/2} \qquad \text{and} \qquad -k_2 \cdot B \cdot \sin\left(k_2 \frac{L}{2}\right) = -k_1 \cdot C \cdot e^{-k_1 \cdot L/2}$$

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 1st 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 $\mathrm{x_0}$. Any displacement from equilibrium results in a linear restoring force: $\mathrm{F} = -\frac{\partial \mathrm{V}}{\partial \mathrm{x}} = -\mathrm{k_f}(\mathrm{x} - \mathrm{x_0})$, the strength of which is dictated by the spring constant $\mathrm{k_f}$. Since we want to know the potential energy V as a function of the position we note that $\frac{\partial \mathrm{V}}{\partial x} - -F(x)$ and integrate as follows:

$$\int \partial \mathrm{V} = \mathrm{V(x)} = -\int -\mathrm{k_f}(\mathrm{x} - \mathrm{x_0})\partial x = \frac{1}{2}\mathrm{k_f}(\mathrm{x} - \mathrm{x_0})^2$$

To place this in a quantum mechanical context we simply insert the position operator $\hat{\mathrm{x}}$ as so: $\hat{\mathrm{V}} = \frac{1}{2}\mathrm{k_f}(\hat{\mathrm{x}} - \mathrm{x_0})^2$, 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 $\mathrm{x_0}$ from the potential energy operator as shown here:

$$\hat{\mathrm{V}} = \frac{1}{2}\mathrm{k_f}(\hat{\mathrm{x}} - \mathrm{x_0})^2 \rightarrow \frac{1}{2}\mathrm{k_f}\hat{\mathrm{x}}^2$$

The implication is that the position operator $\hat{\mathrm{x}}$ is now interpreted as the bond’s displacement *away* from equilibrium. Thus, a positive $\langle\hat{\mathrm{x}}\rangle$ means that the bond is stretched and a negative $\langle\hat{\mathrm{x}}\rangle$ means compressed. There is one more issue to examine, which is the fact that the kinetic energy operator $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}$ 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: $\mu = \frac{\mathrm{m_1 \cdot m_2}}{\mathrm{m_1 + m_2}}$, where $\mathrm{m_1}$ and $\mathrm{m_2}$ are the masses of atoms 1 and 2, respectively.

13.2.1.1 Wavefunctions. With knowledge of the Schrodinger equation:

υ	H_υ	There is an interesting mathematical relationship that can be demonstrated with Hermite polynomials:
0	1	

1	$\frac{2x}{\alpha}$	$$H_{\upsilon+1} = \frac{2x}{\alpha} \cdot H_{\upsilon} - 2\upsilon \cdot H_{\upsilon-1}$$ This is called a recursion and allows all the Hermite polynomials to be determined with just the first one: $H_{\upsilon=0} = 1$.
2	$\frac{4x^2}{\alpha^2} - 2$	
3	$\frac{8x^3}{\alpha^3} - \frac{12x}{\alpha}$	

Table 13.1 Hermite polynomials.

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2}\psi(x) + \frac{1}{2}k_f\hat{x}^2 \cdot \psi(x) = E \cdot \psi(x)$$

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:

$$\psi_{\upsilon}(x) = N_{\upsilon}H_{\upsilon}e^{-x^2/2\alpha^2}$$

where $\alpha = \left(\frac{\hbar^2}{\mu k_f}\right)^{\frac{1}{4}}$, $\upsilon \rightarrow 0,1,2\,...$ is the principal quantum number, $N_{\upsilon} = \left(\frac{1}{\upsilon! 2^{\upsilon}\alpha\sqrt{\pi}}\right)^{\frac{1}{2}}$ is the normalization constant, and H_{υ} 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.

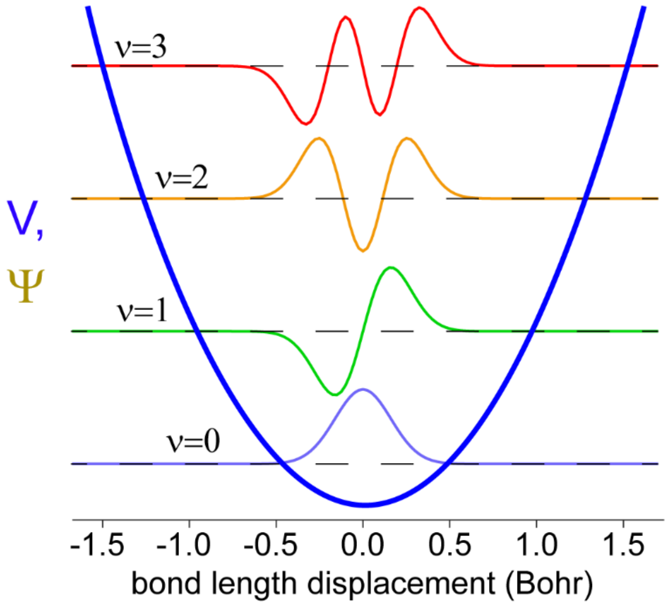


Figure 13.8. The parabolic potential surface (blue line), ground and several excited state wavefunctions for the harmonic oscillator.

There are many other quantum mechanical properties to examine, including the fact that $\langle\hat{x}\rangle = \int \psi_{\upsilon}^{*} \cdot x \cdot \psi_{\upsilon}\, \partial x = 0$ 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 υ reveals the relationship: $\mathrm{E}(\upsilon)=\left(\upsilon+\frac{1}{2}\right)\hbar\omega$, where ω is the angular frequency: $\omega=\left(\frac{\mathrm{k_f}}{\mathrm{mass}}\right)^{\frac{1}{2}}$. An important implication is the fact that the ground state has energy is finite: $\mathrm{E}_{\upsilon=0}=\frac{1}{2}\hbar\omega$. 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, $\mathrm{E}\propto\upsilon$, whereas the particle in a box is quadratic in proportion to its principal quantum number, $\mathrm{E}\propto\mathrm{n}^2$.

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 $\mathrm{k}\sim\mathrm{e}^{-\Delta G^*}$ (like the Arrhenius equation), the relative rates of reaction involving a proton are generally faster to the same with deuterium according to the formula:

$$\frac{\mathrm{k_{CH}}}{\mathrm{k_{CD}}}\sim\frac{\mathrm{e}^{-\Delta G^*_{\mathrm{CH}}}}{\mathrm{e}^{-\Delta G^*_{\mathrm{CD}}}}$$

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.

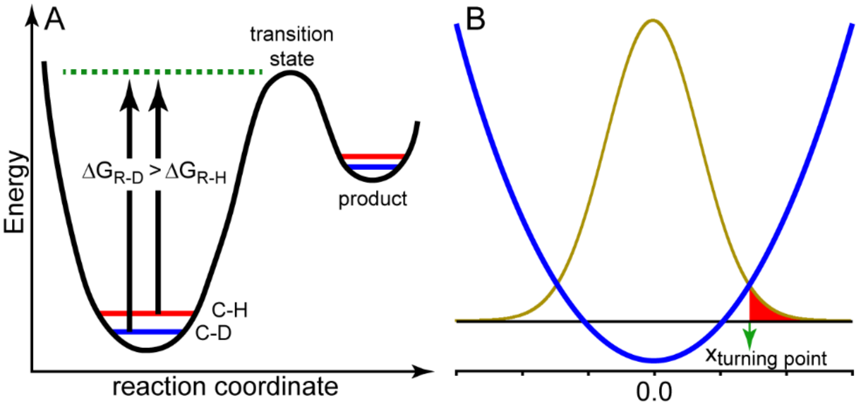


Figure 13.9. A. The kinetic isotope effect is due to the zero-point energy difference between C-H vs. C-D bonds. **B.** A turning point is where the spring has no more kinetic energy.

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:

$$\frac{1}{2}\hbar\omega = \frac{1}{2}k_f \cdot x_{tp}^2 \rightarrow x_{tp} = \pm\sqrt{\frac{\hbar\omega}{k_f}}$$

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:

$$\int_{x_{tp}}^{\infty} |\psi_{\upsilon=0}|^2 \, \partial x = 0.078$$

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 $0 \leq x \leq L$:

$$\psi(x) = \frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-(x-L/2)^2}{4\sigma^2}}$$

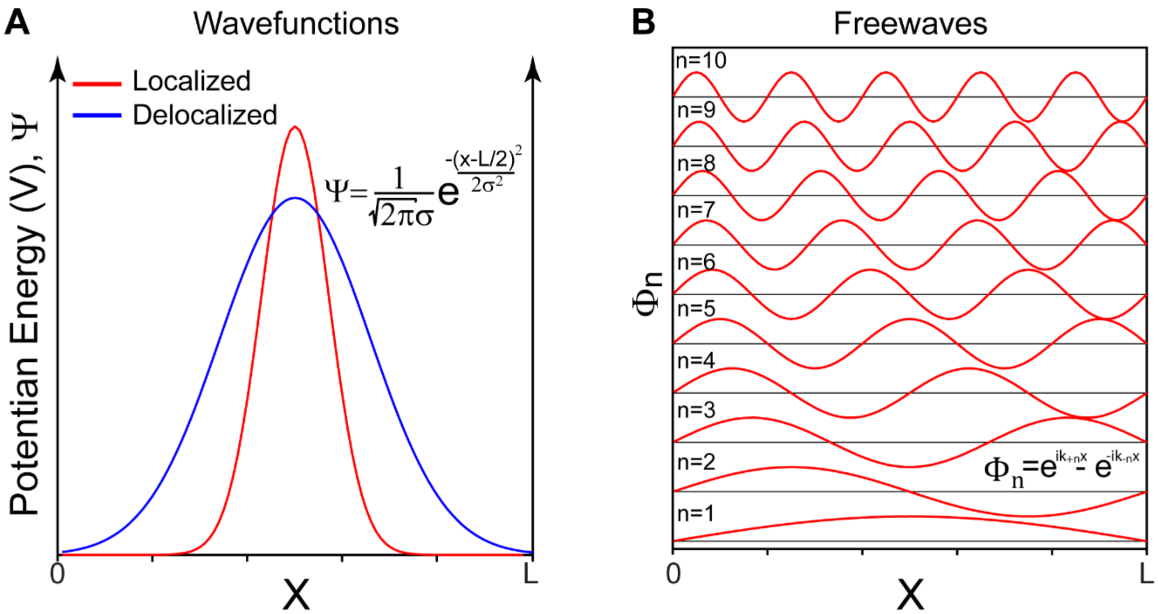


Figure 13.10. A. Localized (red) and delocalized (blue) Gaussian-type wavefunctions have different kinetic energies due to the uncertainty principle. **B**. Freewave states can be summed into a superposition that equates to any other function, such as the localized and delocalized states shown in A.

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 Φ_n of a different operator. This is called a superposition:

$$\psi=\sum_{n} c_n \cdot \Phi_n$$

and for our purposes we will make all the Φ_n's freewave states:

$$\Phi_n=e^{ik_n x}$$

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

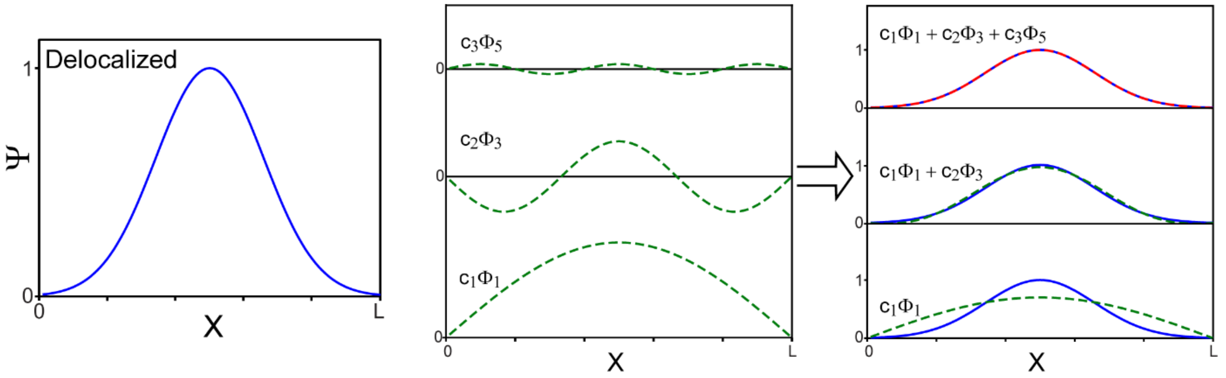


Figure 13.11. A delocalized (blue) Gaussian-type wavefunctions can be constructued by summing several freewave states times appropriate weighing functions. The freewave states must be of even symmetry to contribute. A sum of just three freewaves provide a near-pefect representation of the delocalized state.

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:

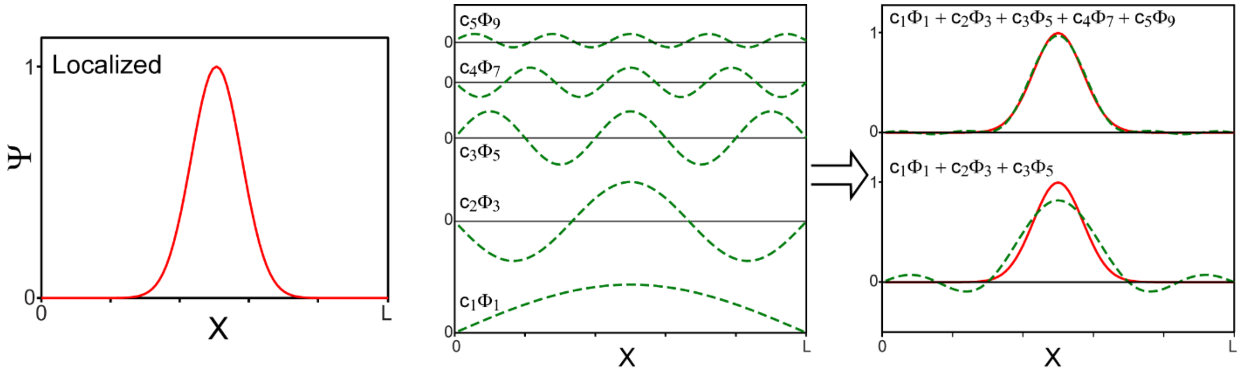


Figure 13.12. A localized (red) Gaussian-type wavefunctions requires the summation of at least 5 free waves to provide a reasonable representation of the original state.

$$\langle p \rangle = |c_1|^2 \cdot \hbar k_1 + |c_2|^2 \cdot \hbar k_3 + |c_3|^2 \cdot \hbar k_5$$

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 (σ) 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:

$$\langle \mathrm{Var}(\hat{x}) \rangle = \langle \frac{1}{N-1} \sum_{i=1}^{N} (x - \bar{x})^2 \rangle = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2$$

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: $\psi(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}}$ using the $\hat{x}$ and $\hat{x}^2$ operators.

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi^* \cdot \hat{x} \cdot \psi \cdot \partial x = \int_{-\infty}^{\infty} \left(\frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \right)^* \cdot x \cdot \frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \partial x$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x \cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}} \cdot \partial x = \frac{L}{2}$$

Next:

$$\langle \hat{x}^2 \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x^2 \cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}} \cdot \partial x = \sigma^2 + \left(\frac{L}{2}\right)^2$$

As a result: $\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2 = \sigma^2 + \left(\frac{L}{2}\right)^2 - \left(\frac{L}{2}\right)^2 = \sigma^2$. 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, $\mathrm{var}(\hat{p}) = \langle p^2 \rangle - \langle p \rangle^2$:

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} \psi^* \cdot \hat{p} \cdot \psi \cdot \partial x = \int_{-\infty}^{\infty} \left(\frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \right)^* \cdot \frac{\hbar}{i} \frac{\partial}{\partial x} \frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \partial x =$$

$$\frac{\hbar}{i\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \frac{\partial}{\partial x} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \partial x = \frac{\hbar}{i\sqrt{8\pi}\sigma^3} \int_{-\infty}^{\infty} \left(x - \frac{L}{2}\right) \cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}} \cdot \partial x = 0$$

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:

$$\langle \hat{p}^2 \rangle = \int_{-\infty}^{\infty} \psi^* \cdot \hat{p}^2 \cdot \psi \cdot \partial x = -\hbar^2 \int_{-\infty}^{\infty} \left(\frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \right)^* \cdot \frac{\partial^2}{\partial x^2} \frac{1}{(2\pi\sigma^2)^{1/4}} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \partial x =$$

$$\frac{-\hbar^2}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \frac{\partial^2}{\partial x^2} e^{\frac{-\left(x-\frac{L}{2}\right)^2}{4\sigma^2}} \cdot \partial x = \frac{-\hbar^2}{\sqrt{32\pi}\sigma^5} \int_{-\infty}^{\infty} \left(\frac{L^2}{4} - 2\sigma^2 - Lx + x^2 \right) \cdot e^{\frac{-\left(x-\frac{L}{2}\right)^2}{2\sigma^2}} \cdot \partial x$$

$$= \frac{\hbar^2}{4\sigma^2}$$

As a result, the variance in momentum is: $\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2 = \frac{\hbar^2}{4\sigma^2} - 0^2 = \frac{\hbar^2}{4\sigma^2}$

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:

$$\mathrm{Var}(\hat{x}) \cdot \mathrm{Var}(\hat{p}) = \sigma^2 \frac{\hbar^2}{4\sigma^2} = \frac{\hbar^2}{4}$$

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: $\vec{a} \cdot \vec{b} = |a||b|\cos(\theta)$, is equal to or less that $|a||b|$ due to the fact that the maximum $\cos(\theta)$ can be is 1. This concept allows us to express the Heisenberg uncertainty principle as an equation:

$$\mathrm{Var}(\hat{x}) \cdot \mathrm{Var}(\hat{p}) \geq \frac{1}{4}|\langle[\hat{x}, \hat{p}]\rangle|^2$$

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:

$$\langle[\hat{x}, \hat{p}]\rangle = \frac{\hbar}{i}\frac{1}{\psi}(x \cdot \psi' - x \cdot \psi' + \psi) = \frac{\hbar}{i}\frac{\psi}{\psi} = \frac{\hbar}{i}$$

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:

$$\mathrm{Var}(\hat{x}) \cdot \mathrm{Var}(\hat{p}) \geq \frac{\hbar^2}{4}$$

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: $\mathrm{E} \propto \frac{1}{\mathrm{L}^2}$. 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 $[\hat{\mathrm{x}}, \hat{\mathrm{p}}] = \hat{\mathrm{x}} \cdot \hat{\mathrm{p}} - \hat{\mathrm{p}} \cdot \hat{\mathrm{x}}$ can be interpreted in a way that makes sense out of the uncertainty principle. Since $[\hat{\mathrm{x}}, \hat{\mathrm{p}}] \neq 0$, then $\langle \hat{\mathrm{x}} \cdot \hat{\mathrm{p}} \rangle \neq \langle \hat{\mathrm{p}} \cdot \hat{\mathrm{x}} \rangle$, 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 $\mathrm{var}(\hat{\mathrm{x}})$ and $\mathrm{var}(\hat{\mathrm{p}})$ 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: $\mathrm{var}(\hat{\mathrm{x}}) \cdot \mathrm{var}(\hat{\mathrm{p}}) = \frac{\hbar^2}{4}$. 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:

$$\mathrm{Var}(\widehat{\Omega}_1) \cdot \mathrm{Var}(\widehat{\Omega}_2) \geq \frac{1}{4}\left|\langle[\widehat{\Omega}_1, \widehat{\Omega}_2]\rangle\right|^2$$

and as a result there is uncertainty if $[\widehat{\Omega}_1, \widehat{\Omega}_2] \neq 0$. 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:

$$\mathrm{Var}(\hat{x}) \cdot \mathrm{Var}(\widehat{KE}) \geq \frac{\hbar^2}{4m}|\langle\hat{p}\rangle|^2$$

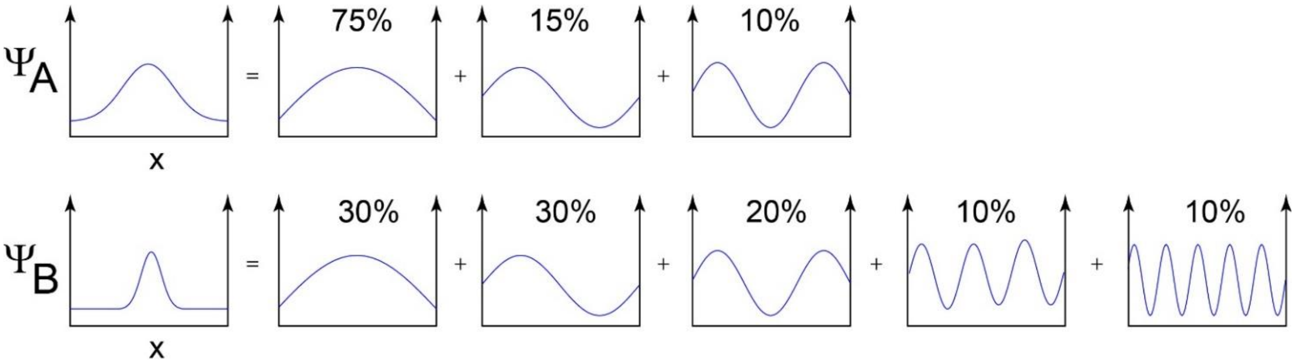
This at first may appear hard to interpret as the commutator is an operator rather than a constant. What is meant here is that the uncertainty between position and kinetic energy is dependent on the expectation of momentum. Thus, if the particle has no momentum then there is a potential for there to 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 $[\widehat{\Omega}_1, \widehat{\Omega}_2] \neq 0$. 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.

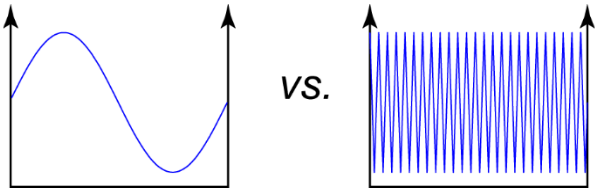
Problems: Numerical

1. In class, I mentioned that the uncertainty principal "does things". Here is what I mean; we decomposed the particle in a box wavefunctions shown below (A & B) into momentum wave eigenstates (i.e. $e^{ik\cdot x}$) as shown below:



Recall that, as the "A" state has more uncertainty in position, it can be decomposed into just a few momentum waves. However, the "B" state requires more momentum waves, perhaps ~100 of them. Also look at the handout for a definitive example that was done with computer analysis.

a. How does the energy of the momentum waves change? Simply state which momentum wave below has more energy and why: **(2 pts)**



b. Given your answer in pt. a, which of the two wavefunctions (the delocalized state "A" or more localized state "B") have more kinetic energy and why? **(8 pts)**

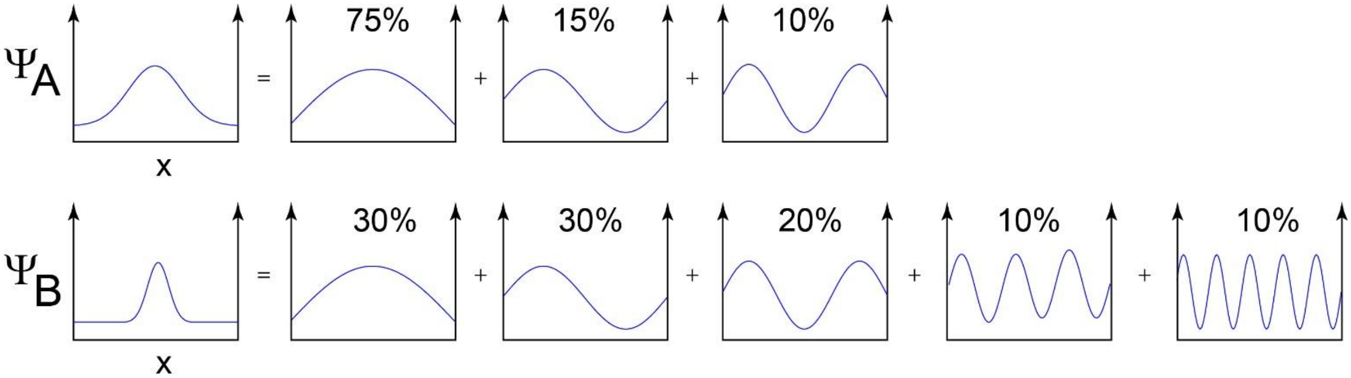
Hint: I have made up a table of components 1→5 that have respective energies of 1 J →5 J, and the percent that each contributes to states A and B. Use these data to find the average values of energies for states A and B, which should give you some insight into how to answer this problem.

Energy (eV)	**%A**	**%B**
1	75%	30%
2	15%	30%
3	10%	20%
4	0%	10%
5	0%	10%

This should help you understand how increasing the percent of higher energy states will affect the total energy.

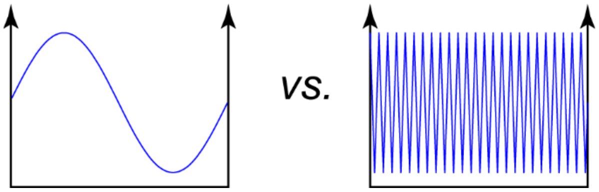
2. In class, I mentioned that the uncertainty principal "does things". Here is what I mean:

We decomposed the particle in a box wavefunctions shown below (A & B) into momentum wave eigenstates (i.e. $e^{ik\cdot x}$) as shown below:



Recall that, as the “A” state has more uncertainty in position, it can be decomposed into just a few momentum waves. However, the “B” state requires more momentum waves, perhaps ~100 of them. Also look at the handout for a definitive example that was done with computer analysis.

a. How does the energy of the momentum waves change? Better yet, just tell me which momentum wave below has more energy and why: **(2 pts)**



b. Given your answer in pt. a, which of the two wavefunctions (the delocalized state “A” or more localized state “B”) have more kinetic energy and why? **(8 pts)**

Hint: I have made up a table of components 1→5 that have respective energies of 1 J →5 J, and the percent that each contributes to states A and B. Use these data to find the average values of energies for states A and B, which should give you some insight into how to answer this problem.

Energy (eV)	**%A**	**%B**
1	50%	30%
2	30%	20%
3	20%	20%
4	0%	15%
5	0%	15%

This should help you understand how increasing the percent of higher energy states will affect the total energy.

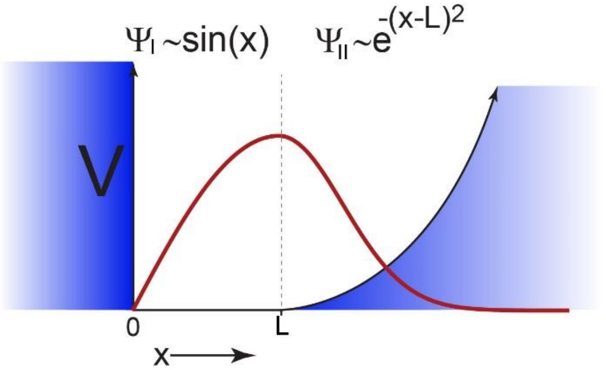
3. HCl gas has an absorption at 2990 cm^{-1}; this is one of the highest frequencies that is known in the infrared spectrum (the IR range is 200 → 13,000 cm^{-1}). Using this information can you estimate the force constant k_f of the spring (bond) that connects the H and Cl? Recall that the energy of a harmonic oscillator is $E = \left(\upsilon + \frac{1}{2}\right)\hbar\omega = \left(\upsilon + \frac{1}{2}\right)\hbar\sqrt{\frac{k_f}{\mu}}$, where μ is the reduced mass: $\mu = \frac{m_1 m_2}{m_1 + m_2}$. ***Hint:*** The ground state has $\upsilon = 0$, and 1 cm^{-1} = 1.986×10^{-23} J. The mass of H is 1 amu and Cl is 35.5 amu. **(7 pts)**

Hint-hint: Did you get ~2050 N/m? Then you forgot that absorption wavelength is due to the ***difference in energy*** between the 1st excited and ground state (final energy – initial energy).

4. Deuterium chloride (DCl) gas has an absorption at 2144 cm^{-1} in the infrared (the IR range is 200 → 13,000 cm^{-1}). Using this information can you estimate the force constant k_f of the spring (bond) that connects the D and Cl? Recall that the energy of a harmonic oscillator is $E = \left(\upsilon + \frac{1}{2}\right)\hbar\omega = \left(\upsilon + \frac{1}{2}\right)\hbar\sqrt{\frac{k_f}{\mu}}$, where μ is the reduced mass: $\mu = \frac{m_1 m_2}{m_1 + m_2}$. ***Hint:*** The ground state has $\upsilon = 0$, and 1 cm^{-1} = 1.986×10^{-23} J. The mass of D is 2 amu and Cl is 35.5 amu.

Hint-hint: Did you get ~2050 N/m? Then you forgot that absorption wavelength is due to the ***difference in energy*** between the 1st excited and ground state (final energy – initial energy). **(7 pts)**

Problems: Theoretical or Explain in Words



1. If I have a potential energy surface as shown on the right, then the solution to the Schrödinger equation to the left of x=L is:

$$\Psi_I(x) = A \cdot \sin\left(\pi \cdot \frac{x}{2L}\right)$$

To the right of x=L is:

$$\Psi_{II}(x) = B \cdot e^{-(x-L)^2}$$

a. Why is the wavefunction in region I a sine function? Why not a cosine function? **(3 pts)**

b. What is the relationship between constants A and B? **(3 pts)**

Hint: This is a derivation question, and the wavefunctions must be continuous. Thus, the "right" wavefunction must equal the "left" one at x=L.

c. Show that the wavefunctions are smooth at x=L. **(3 pts)**

Hint: Now that you know how A is related to B, you can show that the derivatives of the wavefunctions are equal at x=L.

2. If I have a potential energy surface as shown on the right, then the solution to the Schrödinger equation to the left of x=0 is:

$$\Psi_I(x) = A \cdot \cos\left(\pi \cdot \frac{x}{2L}\right)$$

To the right of x=0 is:

$$\Psi_{II}(x) = B \cdot e^{-x^2}$$

a. Why is the wavefunction in region I a cosine function? Why not a sine function? **(3 pts)**

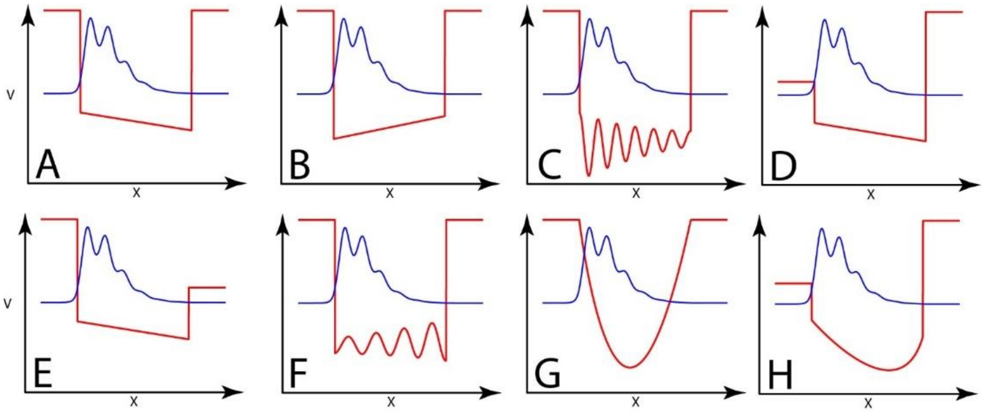
b. What is the relationship between constants A and B? **(3 pts)**

Hint: This is a derivation question, and the wavefunctions must be continuous. Thus, the "right" wavefunction must equal the "left" one at x=0.

c. Show that the wavefunctions are smooth at x=0. **(3 pts)**

Hint: Now that you know how A is related to B, you can show that the derivatives of the wavefunctions are equal at x=0.

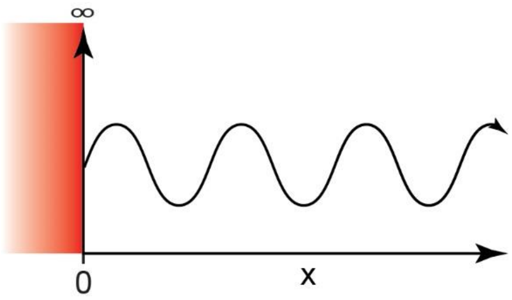
3. I have calculated a wavefunction, in blue, for one of the potential surfaces (red) below. Only one of them is correct-can you identify which potential function is correct and please state why? **(7 pts)**



4. For a free wave hitting a barrier:

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2}$$

were k_1 is real since $k_1 = \frac{\sqrt{2mE}}{\hbar}$ and E is a positive number. However, if E<V, then: $k_2 = \frac{\sqrt{2m(E-V)}}{\hbar}$ and is imaginary and can be expressed as $k_2 = i \cdot k_2' = i \cdot \frac{\sqrt{2m(V-E)}}{\hbar}$ (note how V and E have switched place when "i" is added). The equation for reflection is then: $\frac{B}{A} = \frac{k_1 - i \cdot k_2'}{k_1 + i \cdot k_2'}$. Since the percent reflection is actually $\frac{|B|^2}{|A|^2} = \frac{B^*B}{A^*A}$, please show that reflection is always 100% if E<V. **(5 pts)**



5. Consider the following potential energy surface that has an infinite potential at x=0:

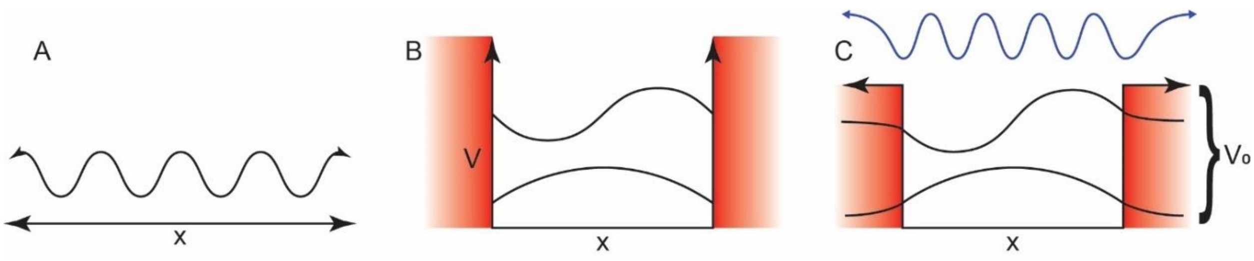
a. Which of the wavefunctions below is the correct for region I and why? **(5 pts)**

1. $\cos(k \cdot x)$ 2. $\text{Sin}(k \cdot x)$ 3. E^{ikx} 4. E^{-ikx}

b. Is there any boundary condition that dictates what k is? In other words, can k take on any value so long at the correct form (question a) is determined? **(3 pts)**

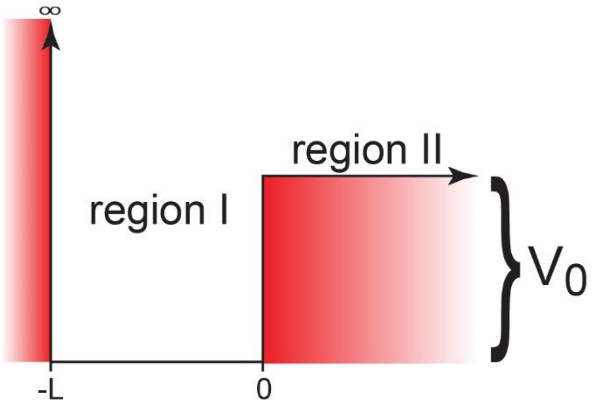
c. If there is no boundary condition that limits the value of k, are there limits on the energy? Please explain, and hint: this is basically a freewave problem. **(3 pts)**

6. The "quantum" in quantum mechanics describes when only certain energy levels are allowed. Thus, there are finite energy differences between the ground state and other excited states. Not all systems have quantized energy levels. Look at the figure below and try to answer the following questions: **(9 pts)**



a. For the free wave: is energy quantized? **b.** What about the particle in a box? **c.** What about the particle in a finite box, if the energy is > V_0 (like the blue wave)?

7. The “half-baked well” potential has infinite potential energy at x=-L, and a step at x=0:



a. Which wavefunction below is the correct for region I and why? Hint: what stipulation does the infinite potential place on the wavefunction?

1. $\cos\left(k_1\{x+L\}-\frac{\pi}{2}\right)$ 2. $\sin(k_1\cdot x)$

3. e^{ik_1x} 4. e^{-ik_1x} **(5 pts)**

b. In the 1st region, since V=0 the Schrödinger equation is:

$$\frac{\hbar^2k_1^2}{2m}\cdot\Psi_I(x)=E\cdot\Psi_I(x)$$

Solve for k_1. Hint: this is just an algebra problem. **(2 pts)**

c. In the 2nd region where the potential step $V=V_0$ exists:

$$\frac{\hbar^2k_2^2}{2m}\cdot\Psi_{II}(x)=(E-V_0)\cdot\Psi_{II}(x)$$

Solve for k_2 in this case. **(2 pts)**

d. The wavefunction $\Psi_{II}(x)$ is in a region of constant potential, therefore possible wavefunctions are:

1. $\cos\left(k_2\{x+L\}-\frac{\pi}{2}\right)$ 2. $\sin(k_2\cdot x)$ 3. e^{ik_2x} 4. e^{-ik_2x}

Figuring out which one is correct is a bit harder. Here is how you reason through it: if a particle passes through the wall from region 1 into region 2, it will continue moving to the right and do so forever since there are no more walls to bounce off of. Therefore, which of the functions above (1-4) correctly describe a particle always moving right?

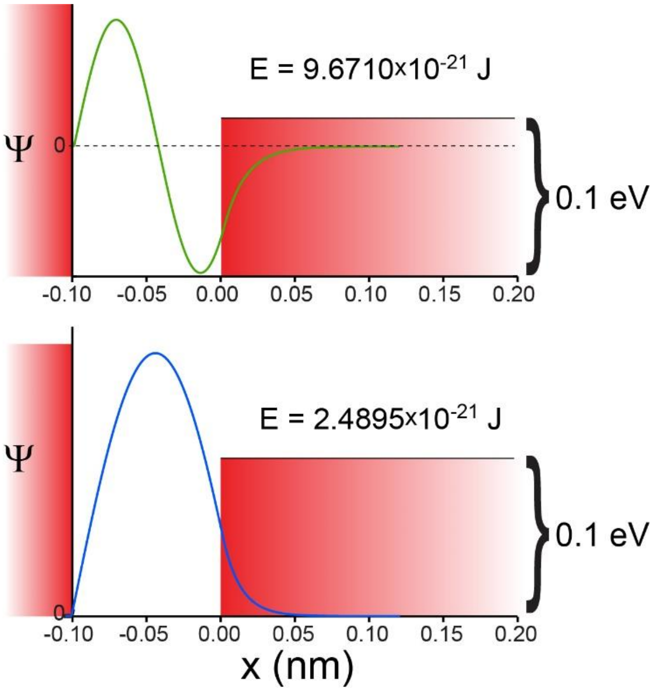
(5 pts)

e. Now unfortunately we run into two possible solutions for region 2. Let’s say that in region 2: $k_2=\frac{\sqrt{2m(E-V_0)}}{\hbar}$, and thus the two possibilities are that the particle has more energy that the potential barrier $(E>V_0)$ or it has less $(E<V_0)$. In the former case $(E>V_0)$, $\Psi_{II}(x)=e^{i\frac{\sqrt{2m(E-V_0)}}{\hbar}x}$ which is a wave that travels to the right forever.

If the energy is less than the potential energy, can you justify substituting $k_2=i\frac{\sqrt{2m(V_0-E)}}{\hbar}$ for $\frac{\sqrt{2m(E-V_0)}}{\hbar}$? Please explain. **(2 pts)**

f. If you plug $k_2=i\cdot\frac{\sqrt{2m(V_0-E)}}{\hbar}$ into $\Psi_{II}(x)=e^{ik_2x}$, does the wavefunction continue to oscillate like a sine or cosine or does it behave differently? Please explain your answer. **(4 pts)**

8. I have drawn here two wavefunctions that are solutions to the half-baked well if the energy of the particle is less than V_0. Obviously, the wavefunctions are continuous and smooth, which is due to using the “right” energies. To show that this is the case, let’s do the following:



a. Set:

$$\Psi_I(x) = \cos\left(\frac{\sqrt{2mE}}{\hbar}\{x+L\} - \frac{\pi}{2}\right)$$

and:

$$\Psi_{II}(x) = e^{\frac{-\sqrt{2m(V_0-E)}}{\hbar}\cdot x}$$

equal at x=0. **(2 pts)**

b. Calculate the derivative of $\Psi_I(x)$ and $\Psi_{II}(x)$, and set the two derivatives equal at x=0. **(6 pts)**

c. Divide the equation in **b** by the equation in **a** to derive the relationship:

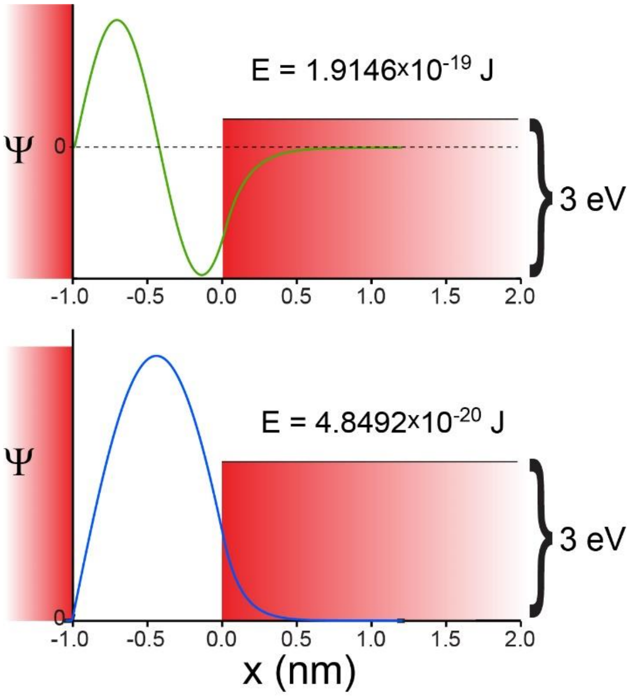
$$\tan\left(\frac{\sqrt{2mE}}{\hbar}L - \frac{\pi}{2}\right) = \frac{\sqrt{(V_0-E)}}{\sqrt{E}}$$

This equation does not allow one to solve for E analytically. Basically, you have to plug in numbers for L, m, and V_0 and then determine what energy E makes the left side equals the right side. **(6 pts)**

d. If the mass of the particle is that of an electron, L is 1 nm, and the barrier is 3 eV, can you show that energies E of 4.8492×10^{-20} J and 1.9146×10^{-19} J (the same shown in the figure) satisfy the relationship in pt. c? **(4 pts)**

e. Drawn above are the two wavefunctions for the states with E =4.8492×10^{-20} J and the other with E =1.9146×10^{-19} J. How would you describe these two states to a student in freshman chemistry? **(4 pts)**

9. I have drawn here two wavefunctions that are solutions to the half-baked well if the energy of the particle is less than V_0. Obviously, the wavefunctions are continuous and smooth, which is due to using the "right" energies. To show that this is the case, let's do the following:



a. Set:

$$\Psi_I(x) = \cos\left(\frac{\sqrt{2mE}}{\hbar}\{x+L\} - \frac{\pi}{2}\right)$$

and:

$$\Psi_{II}(x) = e^{\frac{-\sqrt{2m(V_0-E)}}{\hbar}\cdot x}$$

equal at x=0. **(2 pts)**

b. Calculate the derivative of $\Psi_I(x)$ and $\Psi_{II}(x)$, and set the two derivatives equal at x=0. **(6 pts)**

c. Divide the equation in **b** by the equation in **a** to derive the relationship:

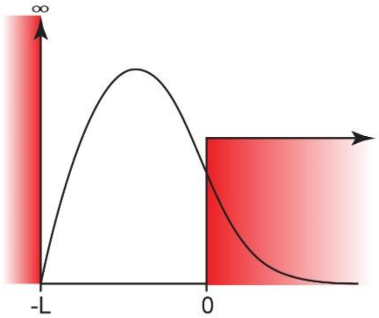
$$\tan\left(\frac{\sqrt{2mE}}{\hbar}L - \frac{\pi}{2}\right) = \frac{\sqrt{(V_0 - E)}}{\sqrt{E}}$$

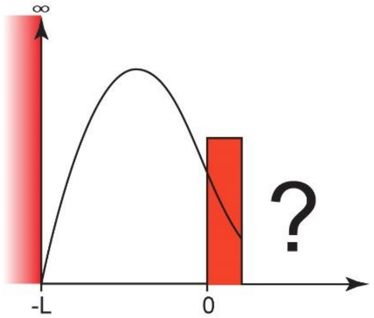
This equation does not allow one to solve for E analytically. Basically, you have to plug in numbers for L, m, and V_0 and then determine what energy E makes the left side equals the right side. **(6 pts)**

d. If the mass of the particle is that of a proton, L is 0.1 nm, and the barrier is 0.1 eV, can you show that energies E of 2.4895×10^{-21} J and 9.6710×10^{-21} J (the same shown in the figure) satisfy the relationship in pt. c? **(4 pts)**

e. Drawn above are the two wavefunctions for the states with E $=2.4895\times10^{-21}$ J and the other with E $=9.6710\times10^{-21}$ J. How would you describe these two states to a student in freshman chemistry? **(4 pts)**

10. In the particle-in-a-half-baked-well problem, you see that the wavefunction decayed exponentially into the barrier when E<V as shown on the left. Now the question is- what do you think happens if the right barrier was “thin”, such that the wavefunction doesn’t decay to 0 before the end of the barrier as shown here? Please draw and explain your result. **(5 pts)**



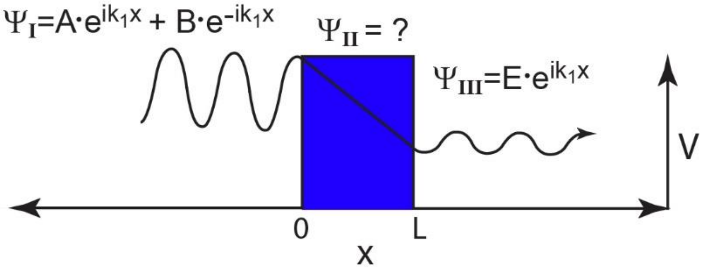


11. Units! a. In a previous problem, an electron (mass$=9.109\times10^{-31}$ kg) was trapped in a 1 nm ($L=1\times10^{-9}$ m), 3 eV ($V_0= 4.807\times10^{-19}$ J) potential well. I gave you the ground and excited state energies (4.85×10^{-20} J and 1.91×10^{-19} J), which I found with: $\tan\left(\frac{\sqrt{2\text{mass}\cdot E}}{\hbar}\cdot L - \frac{\pi}{2}\right) = \frac{\sqrt{(V_0-E)}}{\sqrt{E}}$ using the Wolfram zeros calculator.

Now you do the same- please use the equation, with SI units inputted to find the energies that solve the expression above. ($\hbar = 1.0546\times10^{-34}\,\text{J}\cdot\text{s}$) **Hint:** to answer just send us a screen clip of the website, and most important the website won’t work so don’t try too hard! **(3 pts)**

b. The website won’t return any values because the input parameters are too small. To resolve the problem you are going to use atomic units, in which $\hbar = 1$, $\frac{1}{4\pi\epsilon_0} = 1$, $e^2 = 1$ (the charge of an electron), length is in Bohrs (=0.0529 nm), and the mass of an electron is: $m_e = 1$. In this system of units energy is in Hartrees, where 1 Hartree = 27.2114 eV = 4.36×10^{-18} J. So, if you do the conversions, and re-insert into the $\tan\left(\frac{\sqrt{2\text{mass}\cdot E}}{\hbar}\cdot L - \frac{\pi}{2}\right) = \frac{\sqrt{(V_0-E)}}{\sqrt{E}}$ equation, the website should return the correct answers; please send us a screen shot and verify that the energies are the same as the ones I gave. ***Hint:*** the website can crash if you put in more than three significant figures. **(7 pts)**

12. Concerning the finite barrier problem, let’s think about what happens when a particle hits a barrier (region II) with the same amount of energy as the potential energy barrier, i.e. E=V. Free wavefunctions in the presence of a flat potential are the solution to:



$$\hat{H}\Psi = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x) + V\cdot\Psi(x) = E\cdot\Psi(x)$$

which is simplified into:

$$\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\Psi(\mathrm{x}) = (\mathrm{E}-\mathrm{V})\cdot\Psi(\mathrm{x})$$

For region II, the wavefunction has a general solution of the form: $\Psi(\mathrm{x}) = \mathrm{C}\cdot \mathrm{e}^{\mathrm{i}\cdot \mathrm{k}_2\cdot \mathrm{x}} + \mathrm{D}\cdot \mathrm{e}^{-\mathrm{i}\cdot \mathrm{k}_2\cdot \mathrm{x}}$, where C and D are constants and k$_2$ is defined as: $\mathrm{k}_2 = \frac{\sqrt{2\mathrm{m}(\mathrm{E}-\mathrm{V})}}{\hbar}$.

It turns out that, if E=V, then $\Psi_{\mathrm{II}}(\mathrm{x}) = \mathrm{C}+\mathrm{D}\cdot \mathrm{x}$. Can you show that this wavefunction is a solution to $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\Psi(\mathrm{x}) = (\mathrm{E}-\mathrm{V})\cdot\Psi(\mathrm{x})$? **(5 pts)**

13. In the previous problem of the finite barrier when E=V, we need to solve what is the probability of reflection and transmission. To do so, we must solve a system of four equations- the continuity and smoothness of the wavefunctions Ψ_{I} & Ψ_{II} at x=0 and the same for Ψ_{II} and Ψ_{III} at x=L.

a. If $\Psi_{\mathrm{I}}(\mathrm{x}) = \mathrm{A}\cdot \mathrm{e}^{\mathrm{i}\cdot \mathrm{k}_1\cdot \mathrm{x}} + \mathrm{B}\cdot \mathrm{e}^{-\mathrm{i}\cdot \mathrm{k}_1\cdot \mathrm{x}}$ and $\Psi_{\mathrm{II}}(\mathrm{x}) = \mathrm{C}+\mathrm{D}\cdot \mathrm{x}$, what are the two equations that stipulate that the wavefunction is continuous and smooth at x=0? **(4 pts)**

b. Now if $\Psi_{\mathrm{II}}(\mathrm{x}) = \mathrm{C}+\mathrm{D}\cdot \mathrm{x}$ and $\Psi_{\mathrm{III}}(\mathrm{x}) = \mathrm{E}\cdot \mathrm{e}^{\mathrm{i}\cdot \mathrm{k}_1\cdot \mathrm{x}}$, what are the two equations that stipulate that the wavefunction is continuous and smooth at x=L? **(4 pts)**

14. Now let's solve the equations we derived in the previous question by insert values. We have already assumed that E=V, and let's use a finite value for $\mathrm{k}_1 = \frac{4\pi}{\mathrm{L}}$. This gives us four equations to work with:

$$\mathrm{A}+\mathrm{B} = \mathrm{C}$$

$$\mathrm{i}\cdot\frac{4\pi}{\mathrm{L}}\cdot \mathrm{A} - \mathrm{i}\cdot\frac{4\pi}{\mathrm{L}}\cdot \mathrm{B} = \mathrm{D}$$

$$\mathrm{C}+\mathrm{D}\cdot \mathrm{L} = \mathrm{E}\cdot \mathrm{e}^{\mathrm{i}\cdot 4\pi}$$

$$\mathrm{D} = \mathrm{i}\cdot\frac{\pi}{\mathrm{L}}\cdot \mathrm{E}\cdot \mathrm{e}^{\mathrm{i}\cdot 4\pi}$$

While we can use and note that $\mathrm{e}^{\mathrm{i}\cdot 4\pi} = 1$ to simplify the above, unfortunately, this system of four equations has 5 unknowns (A, B, C, D, and E). However, if we want the (reflection)$^{1/2}$, that is equal to the ratio of B/A. Likewise, (transmission)$^{1/2}$ is the ratio of E/A. Using this information, we can rewrite the system of equations as:

$$1+\mathrm{r} = \mathrm{C}$$

$$\mathrm{i}\cdot\frac{4\pi}{\mathrm{L}} - \mathrm{i}\cdot\frac{4\pi}{\mathrm{L}}\cdot \mathrm{r} = \mathrm{D}$$

$$\mathrm{C}+\mathrm{D}\cdot \mathrm{L} = \mathrm{t}$$

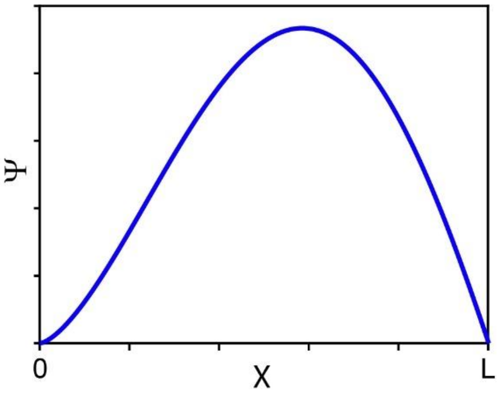
$$\mathrm{D} = \mathrm{i}\cdot\frac{4\pi}{\mathrm{L}}\cdot \mathrm{t}$$

where r=B/A (the square root of the reflectance) and t=E/A (the square root of the transmission). Now you can plug these into the Mathematica Online system of equations solver found here:
http://www.wolframalpha.com/widgets/view.jsp?id=ae438682ce61743f90d4693c497621b7
and determine what r and t are.

When you do, note that you need to take the absolute value of the results for r and t to get the real values like you did in question 3. For example, if you find that $\mathrm{r} = \frac{2\pi}{2\pi+\mathrm{i}}$, then:

$|r|^2 = \left(\frac{2\pi}{2\pi+i}\right)^* \left(\frac{2\pi}{2\pi+i}\right) = \left(\frac{2\pi}{2\pi-i}\right)\left(\frac{2\pi}{2\pi-i}\right) = \frac{4\pi^2}{4\pi^2+1}$ =0.975, which is ~97.5%. Note that 1-$|r|^2$ = $|t|^2$. **(8 pts)**

Hint: Show me what the web site returns of r and t, and then determine the absolute values. Also I found that the Wolfram web site can hang, if so, hit the equal sign as indicated here.



15. Now let's solve the equations we derived in the previous question by insert values. We have already assumed that E=V, and let's use a finite value for $k_1 = \frac{2\pi}{L}$. This gives us four equations to work with:

$$A + B = C$$

$$i \cdot \frac{2\pi}{L} \cdot A - i \cdot \frac{2\pi}{L} \cdot B = D$$

$$C + D \cdot L = E \cdot e^{i \cdot 2\pi}$$

$$D = i \cdot \frac{\pi}{L} \cdot E \cdot e^{i \cdot 2\pi}$$

While we can use and note that $e^{i \cdot 2\pi} = 1$ to simplify the above, unfortunately, this system of four equations has 5 unknowns (A, B, C, D, and E). However, if we want the (reflection)$^{1/2}$, that is equal to the ratio of B/A. Likewise, (transmission)$^{1/2}$ is the ratio of E/A. Using this information, we can rewrite the system of equations as:

$$1 + r = C$$

$$i \cdot \frac{2\pi}{L} - i \cdot \frac{2\pi}{L} \cdot r = D$$

$$C + D \cdot L = t$$

$$D = i \cdot \frac{2\pi}{L} \cdot t$$

where r=B/A (the square root of the reflectance) and t=E/A (the square root of the transmission). Now you can plug these into the Mathematica Online system of equations solver found here:

http://www.wolframalpha.com/widgets/view.jsp?id=ae438682ce61743f90d4693c497621b7

and determine what r and t are. When you do, note that you need to take the absolute value of the results for r and t to get the real values like you did in question 3. For example, if you find that $r = \frac{\pi}{\pi+i}$, then:

$|r|^2 = \left(\frac{\pi}{\pi+i}\right)^* \left(\frac{\pi}{\pi+i}\right) = \left(\frac{\pi}{\pi-i}\right)\left(\frac{\pi}{\pi-i}\right) = \frac{\pi^2}{\pi^2+1}$ =0.908, which is ~91%. Note that 1-$|r|^2$ = $|t|^2$. **(8 pts)**

Hint: Show me what the web site returns of r and t, and then determine the absolute values. Also I found that the Wolfram web site can hang, if so, hit the equal sign as indicated here.

16. For this problem we will evaluate the variance in position $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$ for a wavefunction of the form: $\Psi(x) = \frac{2}{L} \cdot \sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)$ using the following steps:

a. First calculate $\langle x \rangle$ **(6 pts)**

b. Next calculate $\langle x^2 \rangle$ **(6 pts)**

c. And now determine $\langle x^2 \rangle - \langle x \rangle^2$ **(6 pts)**

Hint: $\frac{1}{2} - \frac{3}{2\pi^2} - \left(\frac{2}{3} - \frac{1}{\pi^2}\right)^2 \approx 0.0284$

17. For this problem we will evaluate the variance in momentum $\sigma_p^2 = \langle p^2 \rangle - \langle p \rangle^2$ using the wavefunction: $\Psi(x) = \frac{2}{L} \cdot \sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)$ in the following steps:

a. First determine: $\left(\frac{\hbar}{i}\right) \frac{\partial}{\partial x}\left(\frac{2}{L}\sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)\right)$ **(6 pts)**

b. Set up the $\langle p \rangle$ as: **(4 pts)**

$$\langle p \rangle = \frac{4}{L^2} \int_0^L \left(\sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)\right)^* \left(\frac{\hbar}{i}\right) \frac{\partial}{\partial x}\left(\sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)\right) \cdot \partial x$$

And using your answer from pt. a you should be able to find the answer in the list of identities.

c. Now as for:

$$\langle p^2 \rangle = \frac{4}{L^2} \int_0^L \left(\sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)\right)^* \left(\frac{\hbar^2}{i^2}\right) \frac{\partial^2}{\partial x^2}\left(\sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)\right) \cdot \partial x$$

Unfortunately, this one requires sophisticated mathematical software to solve, from which one finds $\langle p^2 \rangle \approx \frac{11\hbar^2}{L^2}$. From this you can now calculate ${\sigma_p}^2 = \langle p^2 \rangle - \langle p \rangle^2$? **(2 pts)**

18. If the uncertainty principal for position and momentum is: ${\sigma_x}^2 \cdot {\sigma_p}^2 \geq \frac{1}{4} |\langle [\hat{x}, \hat{p}] \rangle|^2 \sim \frac{\hbar^2}{4}$, can you show that this principle is consistent with the σ_x^2 and σ_p^2 determined in the preceding two problems for $\Psi(x) = \frac{2}{L} \cdot \sqrt{x} \cdot \sin\left(\frac{\pi}{L} x\right)$?

(3 pts)

Chapter 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 2nd 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 $\frac{-\hbar^2}{2\cdot\text{mass}}\frac{\partial^2}{\partial x^2}$, 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: $\frac{-\hbar^2}{2\cdot\text{mass}}\frac{\partial^2}{\partial y^2}$ and z: $\frac{-\hbar^2}{2\cdot\text{mass}}\frac{\partial^2}{\partial z^2}$. 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 $\frac{1}{2}k_BT$ 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 $\frac{1}{2}k_BT$ 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 Schrodinger equation for the 3D freewave is then:

$$\frac{-\hbar^2}{2\mathrm{m}}\left(\frac{\partial^2}{\partial \mathrm{x}^2}+\frac{\partial^2}{\partial \mathrm{y}^2}+\frac{\partial^2}{\partial \mathrm{z}^2}\right)\Psi(\mathrm{x},\mathrm{y},\mathrm{z}) = E\cdot\Psi(\mathrm{x},\mathrm{y},\mathrm{z})$$

To make further progress we must know more about the total wavefunction $\Psi(\mathrm{x},\mathrm{y},\mathrm{z})$. Could it be a simple summation of "mini" wavefunctions in different dimensions: $\Psi(\mathrm{x},\mathrm{y},\mathrm{z}) = \Psi_\mathrm{x}(\mathrm{x}) + \Psi_\mathrm{y}(\mathrm{y}) + \Psi_\mathrm{z}(\mathrm{z})$ or perhaps they multiply: $\Psi(\mathrm{x},\mathrm{y},\mathrm{z}) = \Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})$? 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: $\widehat{H}\Psi$ and then divide it out on the left: $\frac{1}{\Psi}\widehat{H}\Psi$. What you are trying to see is if you can write out the Hamiltonian as:

$$\frac{1}{\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})}\widehat{\mathrm{H}}\,\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z}) = \sim\{x\ terms\}+\{y\ terms\}+\{z\ terms\}$$

and, if so, then the total wavefunction is: $\Psi(\mathrm{x},\mathrm{y},\mathrm{z}) = \Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})$.

Separability has two consequences. First, the wavefunction *cannot* look like $\Psi(\mathrm{x},\mathrm{y},\mathrm{z}) \approx \sin(\mathrm{k_x x}+\mathrm{k_y y}+\mathrm{k_z z})$ or $\mathrm{e}^{\mathrm{i}\cdot\mathrm{k}_x\cdot\mathrm{x}}+\mathrm{e}^{\mathrm{i}\cdot\mathrm{k}_y\cdot\mathrm{y}}+\mathrm{e}^{\mathrm{i}\cdot\mathrm{k}_z\cdot\mathrm{z}}$. Second, the method of separability gives us a way to solve the Schrodinger equation as each of the terms becomes a smaller and easier differential equation. Beginning with the definition of separability:

$$\frac{1}{\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})}\left(\frac{-\hbar^2}{2\mathrm{m}}\right)\left(\frac{\partial^2}{\partial \mathrm{x}^2}+\frac{\partial^2}{\partial \mathrm{y}^2}+\frac{\partial^2}{\partial \mathrm{z}^2}\right)\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z}) =$$

$$\frac{1}{\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})}\left(\frac{-\hbar^2}{2\mathrm{m}}\right)\frac{\partial^2}{\partial \mathrm{x}^2}\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z}) +$$

$$\frac{1}{\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})}\left(\frac{-\hbar^2}{2\mathrm{m}}\right)\frac{\partial^2}{\partial \mathrm{y}^2}\Psi(\mathrm{x})\cdot\Psi(y)\cdot\Psi(z) +$$

$$\frac{1}{\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})}\left(\frac{-\hbar^2}{2\mathrm{m}}\right)\frac{\partial^2}{\partial z^2}\Psi_\mathrm{x}(\mathrm{x})\cdot\Psi_\mathrm{y}(\mathrm{y})\cdot\Psi_\mathrm{z}(\mathrm{z})$$

One simple rule of calculus is concerning derivatives is that functions of other variables are not "caught up" by the derivative operation, i.e. $\frac{\partial}{\partial \mathrm{x}} \mathrm{f(x)f(y)} = \mathrm{f(y)} \frac{\partial \mathrm{f(x)}}{\partial \mathrm{x}}$. When we apply that to the 1st term above we find:

$$\frac{1}{\Psi_{\mathrm{x}}(\mathrm{x}) \cdot \Psi_{\mathrm{y}}(\mathrm{y}) \cdot \Psi_{\mathrm{z}}(\mathrm{z})} \left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2}{\partial \mathrm{x}^2} \Psi_{\mathrm{x}}(\mathrm{x}) \cdot \Psi_{\mathrm{y}}(\mathrm{y}) \cdot \Psi_{\mathrm{z}}(\mathrm{z})$$

$$= \frac{\Psi_{\mathrm{y}}(\mathrm{y}) \cdot \Psi_{\mathrm{z}}(\mathrm{z})}{\Psi_{\mathrm{x}}(\mathrm{x}) \cdot \Psi_{\mathrm{y}}(\mathrm{y}) \cdot \Psi_{\mathrm{z}}(\mathrm{z})} \left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2}{\partial \mathrm{x}^2} \Psi_{\mathrm{x}}(\mathrm{x})$$

which simplifies to $\frac{1}{\Psi_{\mathrm{x}}(\mathrm{x})} \left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2 \Psi(\mathrm{x})}{\partial \mathrm{x}^2}$. Appling these across-the-board yields:

$$\left\{\frac{1}{\Psi_{\mathrm{x}}(\mathrm{x})} \left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2 \Psi_{\mathrm{x}}(\mathrm{x})}{\partial \mathrm{x}^2}\right\} + \left\{\frac{1}{\Psi_{\mathrm{y}}(\mathrm{y})} \left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2 \Psi_{\mathrm{y}}(\mathrm{y})}{\partial y^2}\right\} + \left\{\frac{1}{\Psi_{\mathrm{z}}(\mathrm{z})} \left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2 \Psi_{\mathrm{z}}(\mathrm{z})}{\partial z^2}\right\}$$

Success! We see three distinct terms, whereby only an x appears in the 1st one and so on. Furthermore, each term is now a min-Schrodinger 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: $\widehat{\mathrm{H}}\Psi = \mathrm{E}\Psi$ and dividing out the wavefunction on the left $\frac{1}{\Psi} \widehat{\mathrm{H}}\Psi = \frac{1}{\Psi} \mathrm{E}\Psi = \frac{\Psi}{\Psi} \mathrm{E} = \mathrm{E}$. 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: $\mathrm{E} = \mathrm{E}_{\mathrm{x}} + \mathrm{E}_{\mathrm{y}} + \mathrm{E}_{\mathrm{z}}$, and then give each energy to the corresponding term (and using a little algebra to bring the wavefunctions to the right):

$$\left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2}{\partial \mathrm{x}^2} \Psi_{\mathrm{x}}(\mathrm{x}) = \mathrm{E}_{\mathrm{x}} \Psi_{\mathrm{x}}(\mathrm{x})$$

$$\left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2}{\partial \mathrm{y}^2} \Psi_{\mathrm{y}}(\mathrm{y}) = \mathrm{E}_{\mathrm{y}} \Psi_{\mathrm{y}}(\mathrm{y})$$

$$\left(\frac{-\hbar^2}{2\mathrm{m}}\right) \frac{\partial^2}{\partial \mathrm{z}^2} \Psi_{\mathrm{z}}(\mathrm{z}) = \mathrm{E}_{\mathrm{z}} \Psi_{\mathrm{z}}(\mathrm{z})$$

Each of these are simply freewave Schrodinger equations. We know from the last chapter that the solutions are: $\Psi_{\mathrm{x}}(\mathrm{x}) = \mathrm{e}^{\pm \mathrm{i} \cdot \mathrm{k}_x \cdot \mathrm{x}}$, etc., which means that the full solution is:

$$\Psi(\mathrm{x}, \mathrm{y}, \mathrm{z}) = \mathrm{e}^{\pm \mathrm{i} \cdot \mathrm{k}_x \cdot \mathrm{x}} \cdot \mathrm{e}^{\pm \mathrm{i} \cdot \mathrm{k}_y \cdot \mathrm{y}} \cdot \mathrm{e}^{\pm \mathrm{i} \cdot \mathrm{k}_z \cdot \mathrm{z}}$$

It is interesting to note that three separate momentum components now add to the total like a vector: $\mathrm{k}^2 = \mathrm{k}_{\mathrm{x}}^2 + \mathrm{k}_{\mathrm{z}}^2 + \mathrm{k}_{\mathrm{z}}^2$. This is especially apparent if you use the wavefunction to calculate the total energy:

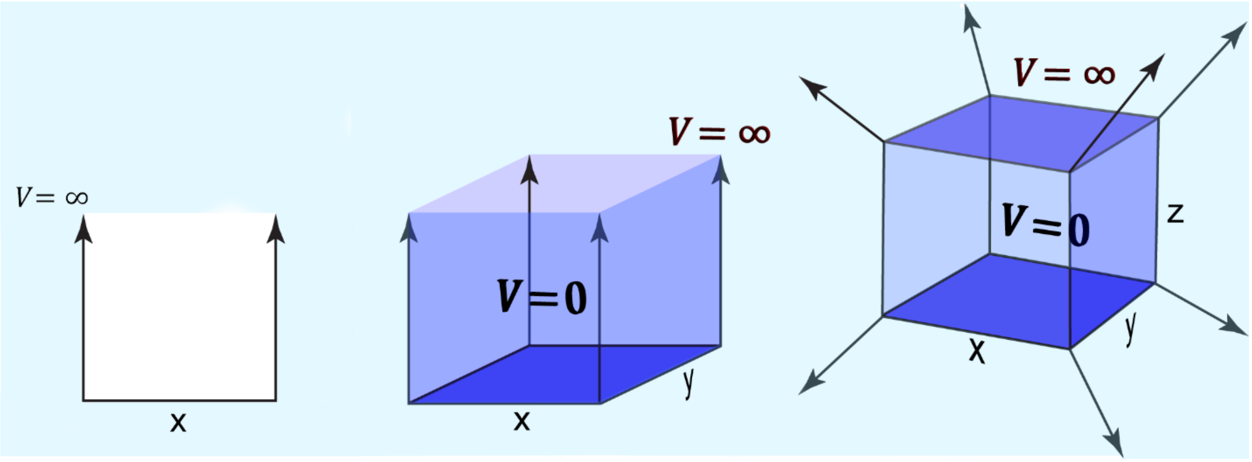


Figure 14.1. Particle in a box potential surfaces from 1D to 3D.

$$E = \frac{\hbar^2}{2\mathrm{m}}(\mathrm{k}_\mathrm{x}^2 + \mathrm{k}_\mathrm{z}^2 + \mathrm{k}_\mathrm{z}^2) = \frac{\hbar^2\mathrm{k}^2}{2\mathrm{m}}$$

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: $\Psi = \sin\left(\frac{\mathrm{n}\pi}{\mathrm{L}}\mathrm{x}\right)$ 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:

$$\Psi_{2\mathrm{D}}(\mathrm{x},\mathrm{y},\mathrm{z}) = \mathrm{N}_{2\mathrm{D}} \cdot \sin(\mathrm{k}_\mathrm{x}\mathrm{x}) \cdot \sin(\mathrm{k}_\mathrm{y}\mathrm{y}) \qquad \Psi_{3\mathrm{D}}(\mathrm{x},\mathrm{y},\mathrm{z}) = \mathrm{N}_{3\mathrm{D}} \cdot \sin(\mathrm{k}_\mathrm{x}\mathrm{x}) \cdot \sin(\mathrm{k}_\mathrm{y}\mathrm{y}) \cdot \sin(\mathrm{k}_\mathrm{z}\mathrm{z})$$

where the normalization constants are $\mathrm{N}_{2\mathrm{D}} = \frac{2}{\sqrt{\mathrm{L}_\mathrm{x}\mathrm{L}_\mathrm{y}}}$, $\mathrm{N}_{3\mathrm{D}} = \frac{2\sqrt{2}}{\sqrt{\mathrm{L}_\mathrm{x}\mathrm{L}_\mathrm{y}\mathrm{L}_\mathrm{z}}}$, and $\mathrm{k}_\mathrm{x} = \frac{\mathrm{n}_\mathrm{x}\pi}{\mathrm{L}_\mathrm{x}}, \mathrm{k}_\mathrm{y} = \frac{\mathrm{n}_\mathrm{y}\pi}{\mathrm{L}_\mathrm{y}}$, and $\mathrm{k}_\mathrm{z} = \frac{\mathrm{n}_\mathrm{z}\pi}{\mathrm{L}_\mathrm{z}}$. 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:

$$\mathrm{E} = \frac{\hbar^2}{2\mathrm{m}}(\mathrm{k}_\mathrm{x}^2 + \mathrm{k}_\mathrm{y}^2 + \mathrm{k}_\mathrm{z}^2) = \frac{\hbar^2\pi^2}{2\mathrm{m}}\left(\frac{\mathrm{n}_\mathrm{x}^2}{\mathrm{L}_\mathrm{x}^2} + \frac{\mathrm{n}_\mathrm{y}^2}{\mathrm{L}_\mathrm{y}^2} + \frac{\mathrm{n}_\mathrm{z}^2}{\mathrm{L}_\mathrm{z}^2}\right)$$

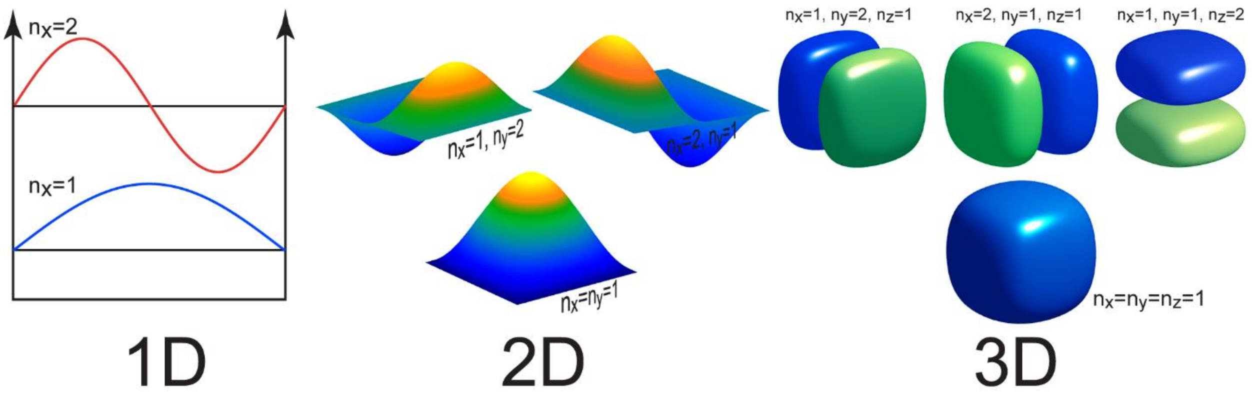


Figure 14.2. How the particle in a box wavefunctions change with increasing dimensionality.

which can be simplified to $E = \frac{\hbar^2\pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$ 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: $n_{x,y,z} = 1,2,3 \ldots$ 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 1st and 2nd excited states; since for example:

$$E = \frac{\hbar^2\pi^2}{2m \cdot L^2}\{(n_x = 2)^2 + 1^2 + 1^2\} = \frac{\hbar^2\pi^2}{2m \cdot L^2}\left\{1^2 + \left(n_y = 2\right)^2 + 1^2\right\}$$

$$= \frac{\hbar^2\pi^2}{2m \cdot L^2}\{1^2 + 1^2 + (n_z = 2)^2\}$$

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: $\frac{-\hbar^2}{2\cdot\mathrm{mass}}\left(\frac{\partial^2}{\partial \mathrm{x}^2}+\frac{\partial^2}{\partial \mathrm{y}^2}+\frac{\partial^2}{\partial \mathrm{z}^2}\right)$, 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 → 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:

$$\widehat{\mathrm{H}}_{2\mathrm{D}}=\frac{-\hbar^2}{2\cdot\mathrm{mass}}\left(\frac{\partial^2}{\partial \mathrm{x}^2}+\frac{\partial^2}{\partial \mathrm{y}^2}\right)$$

This simplifies our transformation problem. The first step is to use the product rule to relate x → r as follows:

$$\frac{\partial}{\partial \mathrm{x}}=\frac{\partial \mathrm{r}}{\partial \mathrm{x}}\frac{\partial}{\partial \mathrm{r}}$$

Cylindrical and Spherical Coordinates

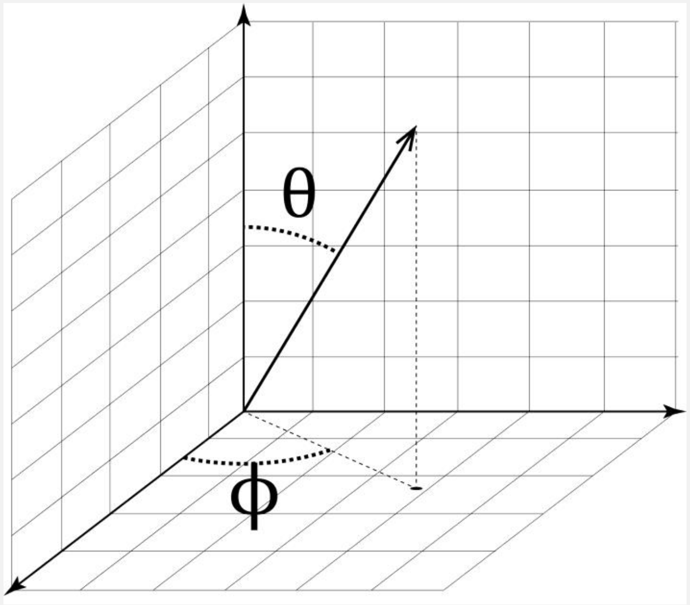


Figure 14.3. Visualization of the polar (θ) and azimuthal (ϕ) angles.

The transformation of Cartesian to cylindrical or spherical coordinates is a dreadful task of recalling high school trigonometry. Rather than reviewing how sine and cosine work and defining the “hypotenuse” (which is, in fact, a large semi-aquatic mammal native to sub-Saharan Africa), instead we simply list the relevant identities without derivations below. Concerning cylindrical coordinates:

$$\mathrm{r} = \sqrt{\mathrm{x}^2 + \mathrm{y}^2}, \phi = \mathrm{atan}\left(\frac{\mathrm{y}}{\mathrm{x}}\right), \mathrm{z} = \mathrm{z}$$

where ϕ is the azimuthal angle. Likewise:

$$\mathrm{x} = \mathrm{r} \cdot \cos(\phi), \mathrm{y} = \mathrm{r} \cdot \sin(\phi), \mathrm{z} = \mathrm{z}$$

Spherical coordinates introduce the θ (polar) angle as follows:

$$\mathrm{r} = \sqrt{\mathrm{x}^2 + \mathrm{y}^2 + \mathrm{z}^2}, \phi = \mathrm{atan}\left(\frac{\mathrm{y}}{\mathrm{x}}\right), \theta = \mathrm{acos}\left(\frac{\mathrm{z}}{\sqrt{\mathrm{x}^2 + \mathrm{y}^2 + \mathrm{z}^2}}\right) = \mathrm{acos}\left(\frac{\mathrm{z}}{\mathrm{r}}\right)$$

Likewise:

$$\mathrm{x} = \mathrm{r} \cdot \sin(\theta)\cos(\phi), \mathrm{y} = \mathrm{r} \cdot \sin(\theta)\sin(\phi), \mathrm{z} = \mathrm{r} \cdot \cos(\theta)$$

However, since x is a function of both r and ϕ we must include the ϕ dependency as well:

$$\frac{\partial}{\partial \mathrm{x}} = \frac{\partial \mathrm{r}}{\partial \mathrm{x}}\frac{\partial}{\partial \mathrm{r}} + \frac{\partial \phi}{\partial \mathrm{x}}\frac{\partial}{\partial \phi}$$

Consequently, the transformation requires us to evaluate $\frac{\partial \mathrm{r}}{\partial \mathrm{x}}$ and $\frac{\partial \phi}{\partial \mathrm{x}}$. Based on the relationships on the previous page, we see that $\mathrm{r} = \sqrt{\mathrm{x}^2 + \mathrm{y}^2}$ and thus:

$$\frac{\partial \mathrm{r}}{\partial \mathrm{x}} = \frac{\partial(\mathrm{x}^2 + \mathrm{y}^2)^{\frac{1}{2}}}{\partial \mathrm{x}} = \frac{1}{2}(\mathrm{x}^2 + \mathrm{y}^2)^{-\frac{1}{2}} \cdot \frac{\partial \mathrm{x}^2}{\partial \mathrm{x}} = \frac{1}{2}\frac{2\mathrm{x}}{(\mathrm{x}^2 + \mathrm{y}^2)^{\frac{1}{2}}} = \frac{\mathrm{x}}{(\mathrm{x}^2 + \mathrm{y}^2)^{\frac{1}{2}}}$$

Recall that we are not here to represent anything with x and y, rather r and ϕ. Thus, we must recognize that $\frac{1}{(\mathrm{x}^2+\mathrm{y}^2)^{\frac{1}{2}}} = \frac{1}{\mathrm{r}}$ and $\mathrm{x} = \mathrm{r} \cdot \cos(\phi)$. Putting this altogether we see:

$$\frac{\partial \mathrm{r}}{\partial \mathrm{x}} = \frac{\mathrm{x}}{(\mathrm{x}^2 + \mathrm{y}^2)^{\frac{1}{2}}} = \frac{1}{\mathrm{r}}\mathrm{r} \cdot \cos(\phi) = \cos(\phi)$$

Likewise, we evaluate $\frac{\partial \phi}{\partial \mathrm{x}}$ as:

$$\frac{\partial \phi}{\partial \mathrm{x}} = \frac{\partial \mathrm{atan}\,(\mathrm{y}/\mathrm{x})}{\partial \mathrm{x}} = -\frac{\sin(\phi)}{\mathrm{r}}$$

Tying this all together reveals:

$$\frac{\partial}{\partial \mathrm{x}} = \cos(\phi)\frac{\partial}{\partial \mathrm{r}} - \frac{\sin(\phi)}{\mathrm{r}}\frac{\partial}{\partial \phi}$$

A similar derivation for the y-coordinate reveals:

$$\frac{\partial}{\partial \mathrm{y}} = \sin(\phi)\frac{\partial}{\partial \mathrm{r}} + \frac{\cos(\phi)}{\mathrm{r}}\frac{\partial}{\partial \phi}$$

The way to transform the kinetic energy operator is to evaluate $\frac{\partial^2}{\partial \mathrm{x}^2}$ and $\frac{\partial^2}{\partial \mathrm{y}^2}$ using the relationships above. The algebra involved isn't difficult but there are a very large number of steps; regardless, the end result is:

$$\widehat{\mathrm{H}} = \frac{-\hbar^2}{2 \cdot \mathrm{mass}} \cdot \left(\frac{\partial^2}{\partial \mathrm{x}^2} + \frac{\partial^2}{\partial \mathrm{y}^2}\right) \rightarrow \frac{-\hbar^2}{2 \cdot \mathrm{mass} \cdot \mathrm{r}^2} \cdot \frac{\partial^2}{\partial \phi^2}$$

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 $\lambda = \mathrm{C}$. We can assume that the other allowed states are n = 4 which has $\lambda = \frac{\mathrm{C}}{2}$ and n = 6 for which $\lambda = \frac{\mathrm{C}}{4}$. From here we can generate an empirical relationship: $\lambda = \frac{\mathrm{L}}{\mathrm{m}}$, where m = 0, 1, 2, … and appears to act like a quantum number. As it is not proper to express this

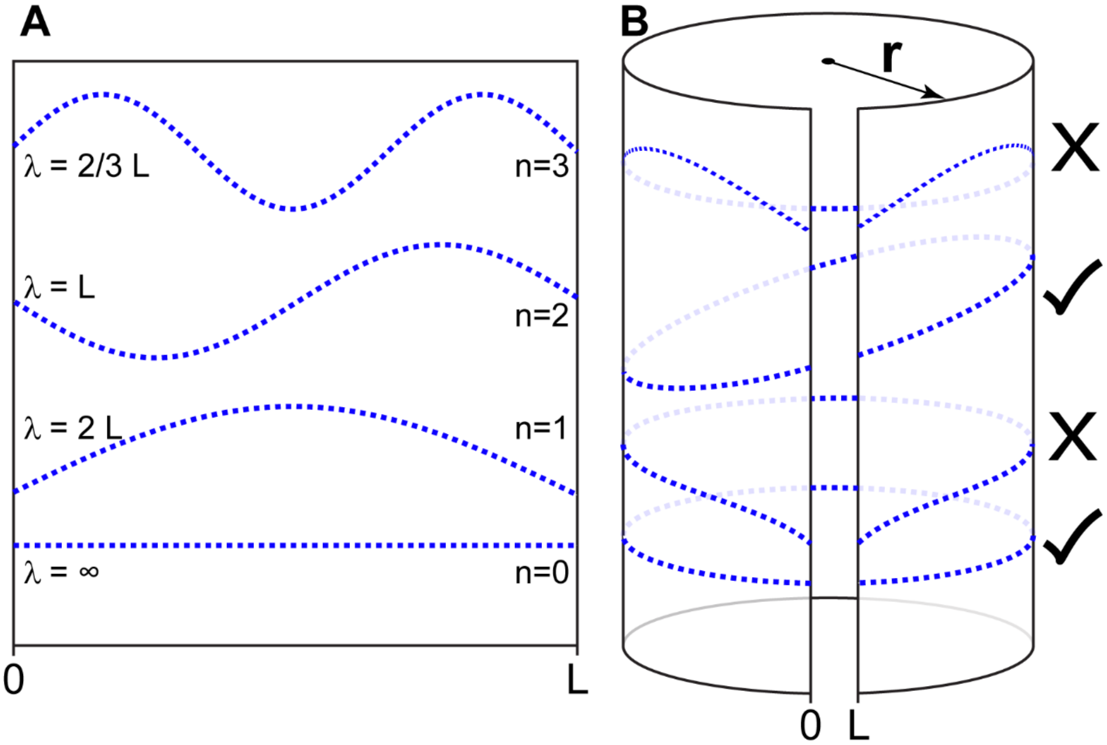


Figure 14.4. A. Particle in a box states (including n=0) provide insight into allowed 2D rigid rotor wavefunctions simply by folding the potential surface over onto itself as seen in **B**.

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:

$$E = \frac{\hbar^2 m^2}{2 \cdot \mathrm{mass} \cdot r^2}$$

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 $I = \mathrm{mass} \cdot r^2$ 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 (Schrodinger) 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:

$$\Psi(\phi) = e^{i\cdot m\cdot \phi}$$

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 $m = \ldots, -2, -1, 0, 1, 2, \ldots$ 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 $\mathrm{x, y, z} \rightarrow \mathrm{r}, \phi, \theta$ step by step beginning with:

$$\frac{\partial}{\partial \mathrm{x}} = \frac{\partial \mathrm{r}}{\partial \mathrm{x}}\frac{\partial}{\partial \mathrm{r}} + \frac{\partial \phi}{\partial \mathrm{x}}\frac{\partial}{\partial \phi} + \frac{\partial \theta}{\partial \mathrm{x}}\frac{\partial}{\partial \theta}$$

and then the same for $\frac{\partial}{\partial \mathrm{y}}$ and $\frac{\partial}{\partial \mathrm{z}}$. 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:

$$\widehat{\mathrm{H}} = \frac{-\hbar^2}{2 \cdot \mathrm{mass}} \cdot \left(\frac{\partial^2}{\partial \mathrm{x}^2} + \frac{\partial^2}{\partial \mathrm{y}^2} + \frac{\partial^2}{\partial \mathrm{z}^2}\right) \rightarrow \frac{-\hbar^2}{2\mathrm{I}} \cdot \left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)$$

where the moment of inertial is defined as before: $\mathrm{I} = \mathrm{mass} \cdot \mathrm{r}^2$. The above Hamiltonian is usually simplified as: $\widehat{\mathrm{H}} = \frac{\hat{\mathrm{L}}^2}{2\mathrm{I}}$, where $\hat{\mathrm{L}}$ 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: $\widehat{\mathrm{H}}\ \psi(\phi)\psi(\theta)$:

$$\frac{-\hbar^2}{2\mathrm{I}} \cdot \left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)\psi(\phi)\psi(\theta) = \mathrm{E} \cdot \psi(\phi)\psi(\theta)$$

Moving the constants to right side makes this look a little easier:

$$\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)\psi(\phi)\psi(\theta) = \frac{-2\mathrm{I} \cdot \mathrm{E}}{\hbar^2} \cdot \psi(\phi)\psi(\theta)$$

And now we divide out the wavefunction on the left side:

$$\frac{1}{\psi(\phi)\psi(\theta)}\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)\psi(\phi)\psi(\theta) = \frac{1}{\psi(\phi)\psi(\theta)}\frac{-2\mathrm{I} \cdot \mathrm{E}}{\hbar^2} \cdot \psi(\phi)\psi(\theta)$$

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 $\psi(\theta)$ yet allows $\psi(\phi)$ to pass through (and vice versa); after some algebra we see that:

$$\frac{1}{\psi(\phi) \cdot \sin^2(\theta)}\frac{\partial^2}{\partial \phi^2}\psi(\phi) + \frac{1}{\psi(\theta) \cdot \sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\psi(\theta) = \frac{-2\mathrm{I} \cdot \mathrm{E}}{\hbar^2}$$

At this point there is a problem with separation because the first part:

Spherical Harmonics

l, m	$Y_{l,m_l} = \psi(\phi)\psi(\theta)$	l, m	$\psi(\phi)\psi(\theta)$
$l = 0$		$l = 2$	
m = 0	$\frac{1}{\sqrt{4\pi}}$	m = -2	$\sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{-2\phi}$
$l = 1$		m = -1	$\sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)e^{-\phi}$
= -1	$\sqrt{\frac{3}{8\pi}}\sin(\theta)e^{-\phi}$	m = 0	$\sqrt{\frac{5}{16\pi}}(3\cos^2(\theta)-1)$
m = 0	$\sqrt{\frac{3}{4\pi}}\cos(\theta)$	m = 1	$-\sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)e^{\phi}$
m = 1	$-\sqrt{\frac{3}{8\pi}}\sin(\theta)e^{\phi}$	m = 2	$-\sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{2\phi}$

Table 14.1. The spherical harmonics, the solutions to the 3D rigid rotor Hamiltonian.

$$\frac{1}{\psi(\phi)\cdot\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\psi(\phi)$$

containing mostly ϕ terms but also has a pesky $\frac{1}{\sin^2(\theta)}$ term. To remove the problem we multiply everything by $\sin^2(\theta)$:

$$\frac{1}{\psi(\phi)}\frac{\partial^2}{\partial\phi^2}\psi(\phi) + \frac{\sin(\theta)}{\psi(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) = \frac{-2I\cdot E}{\hbar^2}\sin^2(\theta)$$

Now we have a clean separation of ϕ and θ terms into mini-Schrodinger equations, although it is interesting to note that the energy is on the θ side:

$$\left(\frac{1}{\psi(\phi)}\frac{\partial^2}{\partial\phi^2}\psi(\phi)\right) + \left(\frac{\sin(\theta)}{\psi(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2I\cdot E}{\hbar^2}\sin^2(\theta)\right) = 0$$

To solve this, we assume that the solution to the ϕ mini-Schrodinger equation (left side) is the same as the 2D rigid rotor that we worked on previously: $\psi(\phi) = \frac{1}{\sqrt{2\pi}}e^{i\cdot m\cdot\phi}$. As a result:

$$\frac{1}{\psi(\phi)}\frac{\partial^2}{\partial\phi^2}\psi(\phi) = \sqrt{2\pi}\cdot e^{-i\cdot m\cdot\phi}\frac{\partial^2}{\partial\phi^2}\frac{1}{\sqrt{2\pi}}e^{i\cdot m\cdot\phi} = -m^2$$

which when inserted into the full equation above we find that:

Example Problem 14.1

Let's verify that $Y_{l=1,m_l=0} = \psi(\theta) = \sqrt{\frac{3}{4\pi}}\cos(\theta) \cdot e^{i \cdot 0 \cdot \phi} = \sqrt{\frac{3}{4\pi}}\cos(\theta)$ is an eigenfunction of the 3D rigid rotor Schrodinger equation:

$$\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2I \cdot E}{\hbar^2}\sin^2(\theta)\psi(\theta) = m^2\psi(\theta)$$

Since m=0 the above simplifies to:

$$\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2I \cdot E}{\hbar^2}\sin^2(\theta) \cdot \psi(\theta) = 0$$

To solve the problem on the left we apply the derivative: $\frac{\partial}{\partial\theta}\cos(\theta) = -\sin(\theta)$ and insert the expression for energy E= $l(l+1)\frac{\hbar^2}{2I} = \frac{\hbar^2}{I}$ because $l = 1$:

$$-\sin(\theta)\frac{\partial}{\partial\theta}\sqrt{\frac{3}{4\pi}}\sin^2(\theta) + 2\sin^2(\theta) \cdot \psi(\theta)$$

Since we know that $\frac{\partial}{\partial\theta}\sin^2(\theta) = 2\sin(\theta)\cos(\theta)$ we find that the left term is:

$$-\sin(\theta)\frac{\partial}{\partial\theta}\sqrt{\frac{3}{4\pi}}\sin^2(\theta) = -2\sin^2(\theta)\left\{\sqrt{\frac{3}{4\pi}}\cos(\theta)\right\} = -2\sin^2(\theta) \cdot \psi(\theta)$$

Putting this altogether:

$$-2\sin^2(\theta) \cdot \psi(\theta) + 2\sin^2(\theta) \cdot \psi(\theta) = 0$$

which is proof that the $Y_{1,0}$ is a valid solution for the 3D Rigid Rotor Hamiltonian.

$$\frac{\sin(\theta)}{\psi(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\psi(\theta) + \frac{2I \cdot E}{\hbar^2}\sin^2(\theta) = m^2$$

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: $l = 0, 1, 2, 3$ .... 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 $m_l = l, (\, l - 1), \ldots 0 \ldots - l$, 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:

$$Y_{l=0,\, m_l=0}(\phi,\theta) = \frac{1}{\sqrt{4\pi}}$$

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 $\left|Y_{l,m_l}(\phi,\theta)\right|^2$ have a specific value, such as $\left|Y_{l,m_l}(\phi,\theta)\right|^2 = 0.95$. 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:

$$E = l(l+1)\frac{\hbar^2}{2I} = 0 \text{ J}$$

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

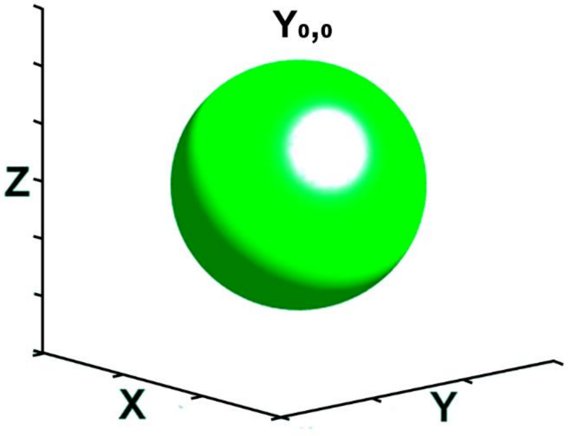


Figure 14.5. The lowest energy s-state $Y_{0,0}$.

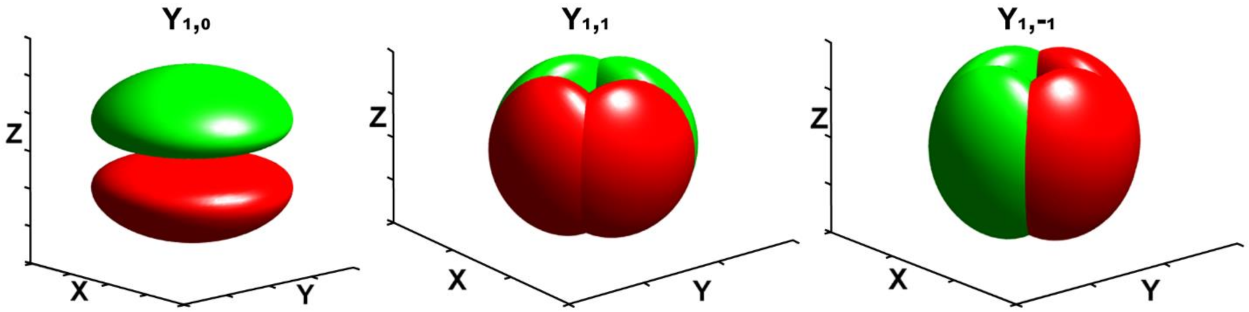


Figure 14.6. There are three p-states due to the triple degeneracy of l =1. While the m$_l$ =0 state likely looks like a hydrogen p_z orbital, the m$_l$ =±1 states are probably less familiar.

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 $m_l = \pm 1$ 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:

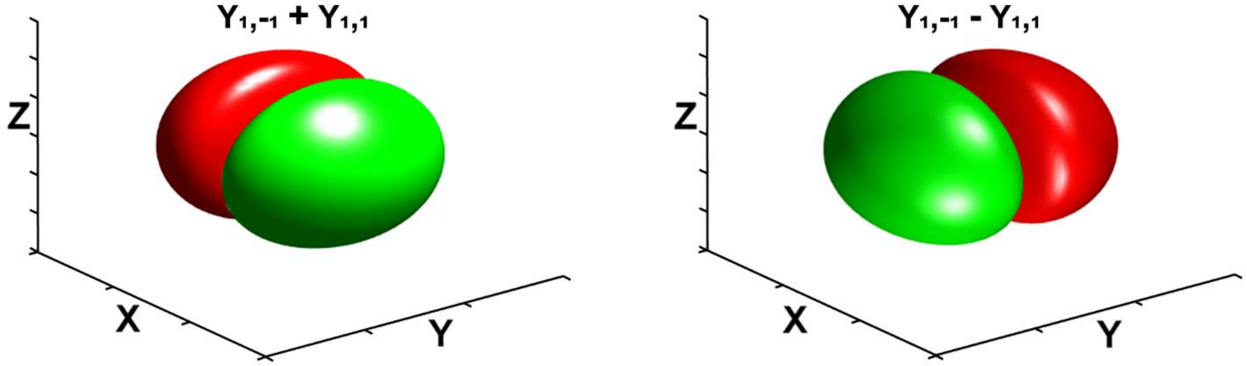


Figure 14.7. Linear combinations of m$_l$ =±1 spherical harmonic wavefunctions return states that appear as the familiar p_x and p_y.

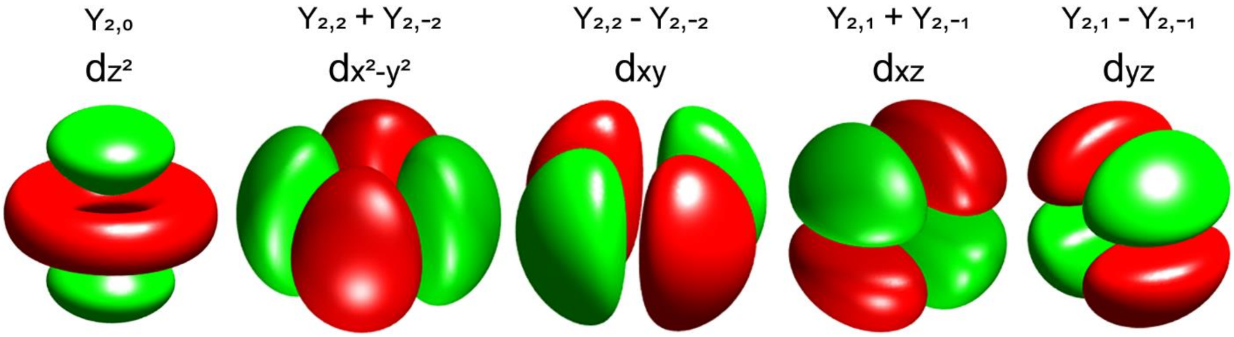


Figure 14.8. Hydrogenic d-orbitals are created from linear combinations of spherical harmonics.

$$\mathrm{Y}_{1,1} + \mathrm{Y}_{1,-1} = \sqrt{\frac{3}{8\pi}}\sin(\theta)\mathrm{e}^{\mathrm{i}\cdot\phi} + \sqrt{\frac{3}{8\pi}}\sin(\theta)\mathrm{e}^{-\mathrm{i}\cdot\phi}$$

Next, collecting terms and using the identity $\mathrm{e}^{-\mathrm{i}\cdot\phi} + \mathrm{e}^{\mathrm{i}\cdot\phi} \sim \cos(\phi)$ yields:

$$\mathrm{Y}_{1,-1} + \mathrm{Y}_{1,1} \sim \sin(\theta)\cos(\phi)$$

If we recall that, for spherical coordinates: $x = \sin(\theta)\cos(\phi)$, which makes $\mathrm{Y}_{1,1} + \mathrm{Y}_{1,-1}$ equal to the p_x orbital. Following the same idea we find that the difference of the two spherical harmonics $\mathrm{Y}_{1,1} - \mathrm{Y}_{1,-1}$can be simplified using $\mathrm{e}^{\mathrm{i}\cdot\phi} - \mathrm{e}^{-\mathrm{i}\cdot\phi} \sim \sin(\phi)$ to:

$$\mathrm{Y}_{1,1} - \mathrm{Y}_{1,-1} \sim \sin(\theta)\sin(\phi)$$

and since $y = \sin(\theta)\sin(\phi)$ then $\mathrm{Y}_{1,1} + \mathrm{Y}_{1,-1}$ 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

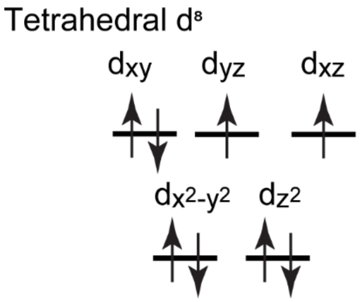


Figure 14.9. The spin up / spin down of electron configurations is due to spin angular momentum.

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 ~2000× 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:

$$\hat{S}_z\alpha = s_z \cdot \alpha = ½\hbar \cdot \alpha \quad \text{and} \quad \hat{S}_z\beta = s_z \cdot \beta = -½\hbar \cdot \beta$$

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:

$$\vec{L} = \vec{r} \times \vec{p}$$

where $\vec{r}$ is the position of the particle, $\vec{p}$ is momentum and reveals the direction of motion, and $\vec{L}$ is the angular momentum vector. As everything is a vector the angular momentum can be decomposed into x, y and z components, i.e. $\vec{L} = \hat{L}_x + \hat{L}_y + \hat{L}_z$ (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 $\vec{L} = \vec{r} \times \vec{p}$ 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:

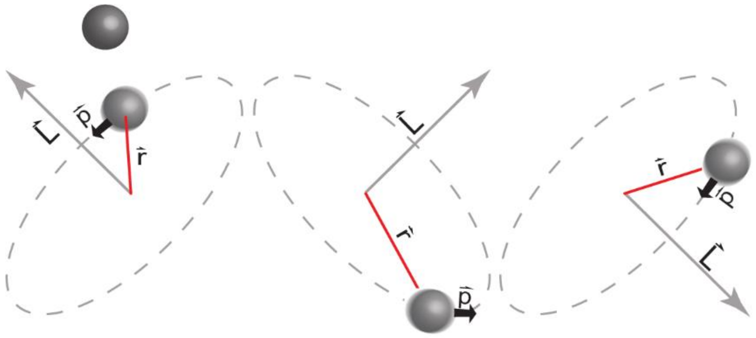


Figure 14.10. The angular momentum vector is like the axel of a wheel that follows the right-hand rule.

$$\hat{L}_x = \frac{\hbar}{i}\left\{y\cdot\frac{\partial}{\partial z} - z\cdot\frac{\partial}{\partial y}\right\},\ \hat{L}_y = \frac{\hbar}{i}\left\{z\cdot\frac{\partial}{\partial x} - x\cdot\frac{\partial}{\partial z}\right\},\text{ and }\ \hat{L}_z = \frac{\hbar}{i}\left\{x\cdot\frac{\partial}{\partial y} - y\cdot\frac{\partial}{\partial x}\right\}$$

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:

$$\frac{\partial}{\partial x} = \sin(\theta)\cos(\phi)\frac{\partial}{\partial r} + \frac{\cos(\theta)\cos(\phi)}{r}\frac{\partial}{\partial \theta} - \frac{\sin(\phi)}{r\cdot\sin(\theta)}\frac{\partial}{\partial \phi}$$

and:

$$\frac{\partial}{\partial y} = \sin(\theta)\sin(\phi)\frac{\partial}{\partial r} + \frac{\cos(\theta)\sin(\phi)}{r}\frac{\partial}{\partial \theta} + \frac{\cos(\phi)}{r\cdot\sin(\theta)}\frac{\partial}{\partial \phi}$$

Hence the angular momentum in the z direction is: $\hat{L}_z = \frac{\hbar}{i}\left\{x\cdot\frac{\partial}{\partial y} - y\cdot\frac{\partial}{\partial x}\right\} = \frac{\hbar}{i}\cdot$

$$\{r\cdot\sin(\theta)\cos(\phi)\cdot\sin(\theta)\sin(\phi)\frac{\partial}{\partial r} + r\cdot\sin(\theta)\cos(\phi)\cdot\frac{\cos(\theta)\sin(\phi)}{r}\frac{\partial}{\partial \theta} + r\cdot\sin(\theta)\cos(\phi)\cdot\frac{\cos(\phi)}{r\cdot\sin(\theta)}\frac{\partial}{\partial \phi}$$
$$-r\cdot\sin(\theta)\sin(\phi)\cdot\sin(\theta)\cos(\phi)\frac{\partial}{\partial r} - r\cdot\sin(\theta)\sin(\phi)\cdot\frac{\cos(\theta)\cos(\phi)}{r}\frac{\partial}{\partial \theta} + r\cdot\sin(\theta)\sin(\phi)\cdot\frac{\sin(\phi)}{r\cdot\sin(\theta)}\frac{\partial}{\partial \phi}\}$$

While this looks overwhelming, note how the first two terms on each line cancel, leaving:

$$\hat{L}_z = \frac{\hbar}{i}\cdot\left\{r\cdot\sin(\theta)\cos(\phi)\cdot\frac{\cos(\phi)}{r\cdot\sin(\theta)} + r\cdot\sin(\theta)\sin(\phi)\cdot\frac{\sin(\phi)}{r\cdot\sin(\theta)}\right\}\frac{\partial}{\partial \phi} =$$
$$\frac{\hbar}{i}\cdot\{\cos^2(\phi) + \sin^2(\phi)\}\frac{\partial}{\partial \phi} = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$$

Very simple! Along the same lines you find that:

$$\hat{L}_x = \frac{\hbar}{i}\left(-\cot(\theta)\cos(\phi)\frac{\partial}{\partial \phi} - \sin(\phi)\frac{\partial}{\partial \theta}\right)$$

and:

$$\hat{L}_y = \frac{\hbar}{i}\left(-\cot(\theta)\sin(\phi)\frac{\partial}{\partial \phi} + \cos(\phi)\frac{\partial}{\partial \theta}\right)$$

The angular kinetic energy can be derived from:

$$\frac{\hat{L}^2}{2I} = \frac{\left(\hat{L}_x + \hat{L}_y + \hat{L}_z\right)^2}{2I} = \frac{-\hbar^2}{2I}\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta}\right)$$

which is exactly the same as shown before.

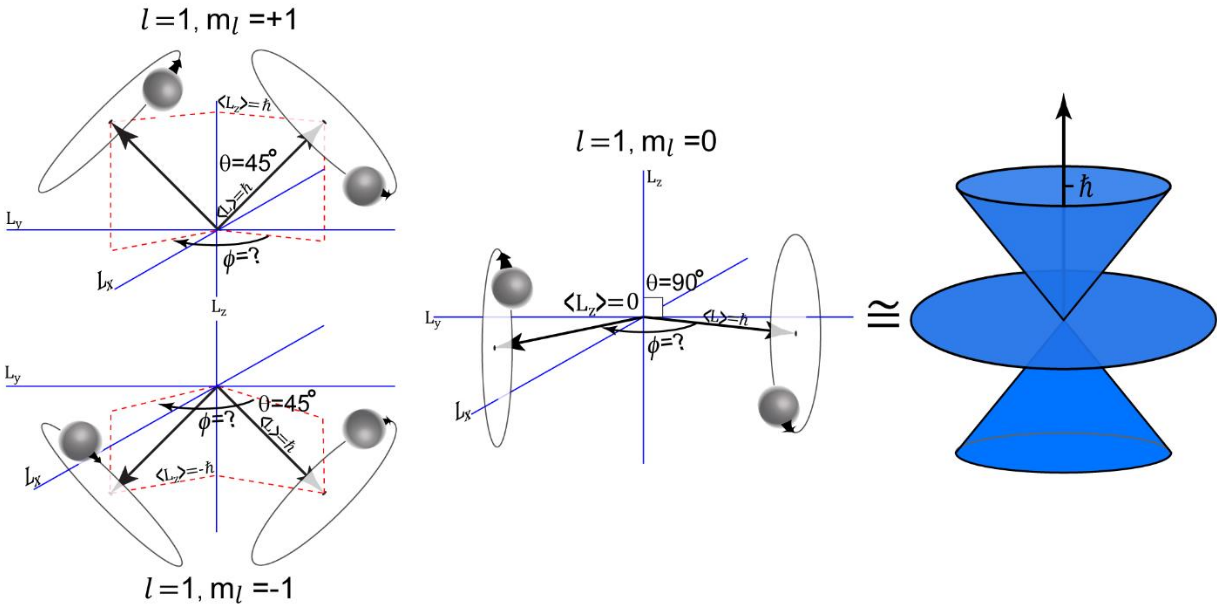


Figure 14.11. The uncertainty principle means that the projection of the angular momentum vector onto the x-y plane is unknown. As a result, the exact motion of the quantum rotor is ill-defined. On the right is a common representation of the angular momentum.

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 Φ is an eigenvector of $\hat{A}$, then $\hat{A}\Phi = \omega\Phi$ where ω is just a constant such as $\hbar$ or 0. However, the eigenvalue equation for won't work for the other operator: $\hat{B}\Phi \neq \omega\Phi$. Hence, whatever observable that $\hat{B}$ describes, you can't know what that is for the state described by Φ. 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: $\left[\hat{L},\hat{L}_x\right] \neq 0$,

$[\hat{L}, \hat{L}_y] \neq 0$, $[\hat{L}_z, \hat{L}_x] \neq 0$, and finally $[\hat{L}_z, \hat{L}_y] \neq 0$. 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.

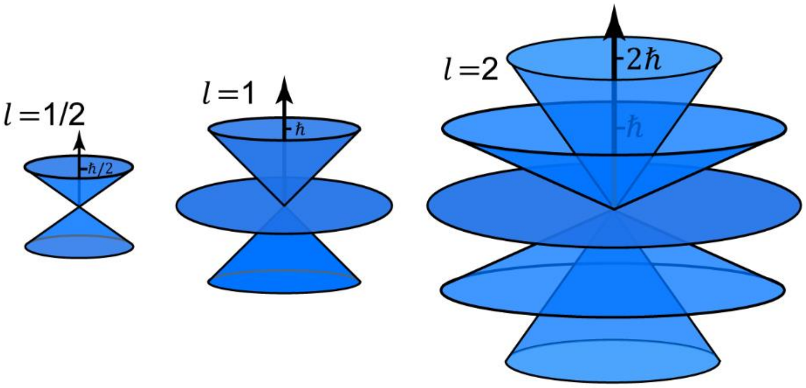


Figure 14.12. The uncertainty principle as applied to various spin systems. The $l=1/2$ system describes the spin of electrons.

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 $\hat{\mathrm{J}}_z$ that has eigenvalues j_z. Similar to the m_l quantum numbers, the allowed values for j_z are:

$$\mathrm{j}, \mathrm{j}-1 \ldots 0 \ldots -\mathrm{j}$$

The wavefunctions of the total angular momentum operators $\hat{\mathrm{J}}$ and $\hat{\mathrm{J}}_z$ 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 $\hat{\mathrm{J}}$, rather $\hat{\mathrm{J}}^2$ 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:

$$\mathrm{j} = l + \mathrm{s}, l + \mathrm{s} - 1 \ldots |l - \mathrm{s}|$$

Take for example a hydrogen atom in a $2\mathrm{p}^1$ excited state. Here, we have to add the spin angular momentum $\mathrm{s} = \frac{1}{2}$ with the orbital momentum $l = 1$. As a result, we can see that there are two possible j states: $\mathrm{j} = l + \mathrm{s} = 1 + \frac{1}{2} = \frac{3}{2}$ and $\mathrm{j} = l - \mathrm{s} = 1 - \frac{1}{2} = \frac{1}{2}$. We can express this information in a quantity called a term symbol: ${}^{2S+1}L_j$; in this example there are two possible states labeled ${}^{2}\mathrm{P}_{3/2}$ and ${}^{2}\mathrm{P}_{1/2}$. It is important to note that there are six possible states for the $2\mathrm{p}^1$ electron configuration because

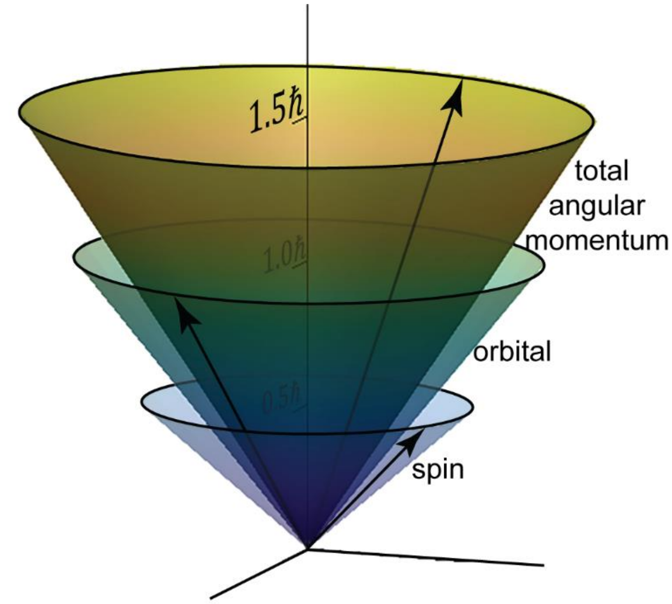


Figure 14.13. Addition of the spin and orbital angular momentum of a 2p electron into a total angular momentum j=3/2 state.

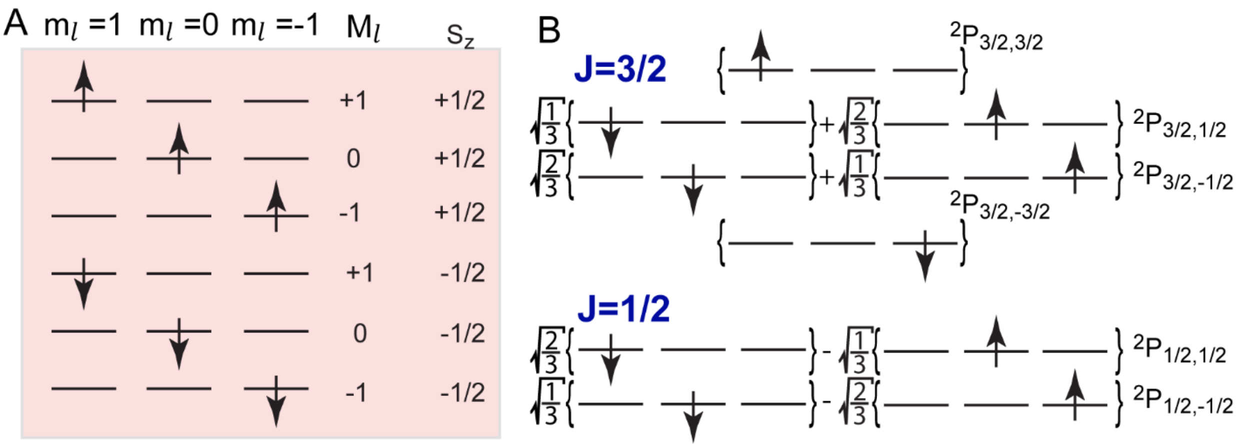


Figure 14.14. A. A hydrogen atom with a $2p^1$ configuration has a single electron in one of possibley three p orbitals. As a result there are six possible states. **B.** Addition of the $l=1$ and s=1/2 angular momentum creates six possibe j states.

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 $^2P_{1/2}$; 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 $1s^12s^1$ 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 ↑↑ is for the +1 sub-s_{tot} state, ↓↓ is for -1 and ↑↓ +↓↑ is for 0. Likewise there is the singlet state with a $s_{\text{tot}} = s_1 - s_2 = 0$, which has the associated spin wavefunction ↑↓ −↓↑. 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.

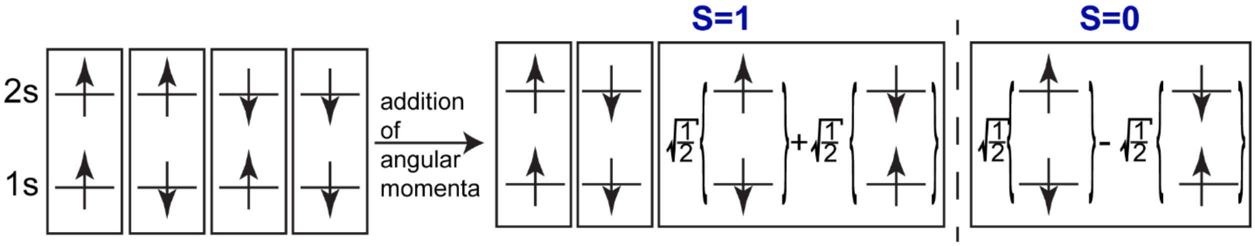
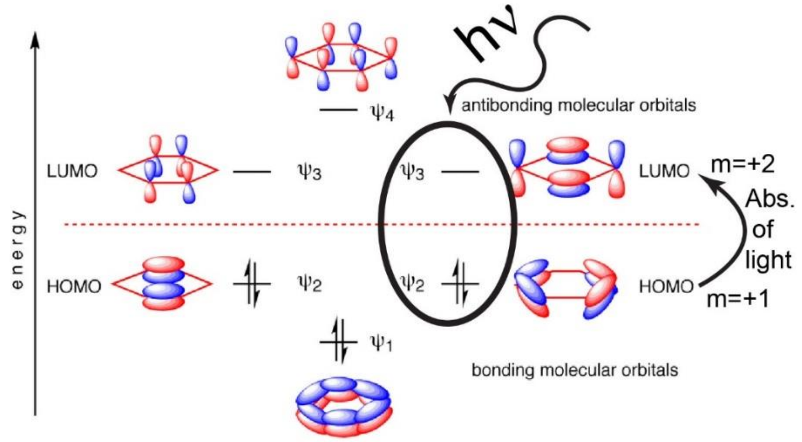
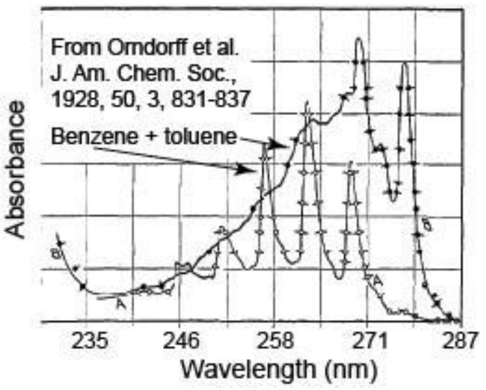


Figure 14.15. Two electrons in s-states with no orbital angular momentum add to form three S=1 (triplet) and one S=0 (singlet) spin states. While nominally degenerate, the triplet state is preferred because of exchange energy, see Ch. 15.

Problems: Numerical

1. a. Shown here are the p-orbitals of benzene’s electrons. The occupied HOMO looks like a 2D rigid rotor m=1 wavefunction, whereas the LUMO is like m=2. If this transition is responsible for the absorption of UV light, what wavelength of photon in nanometers will the electron absorb? The energy of a 2D rigid rotor is $\frac{\hbar^2 \mathrm{m}^2}{2\mathrm{I}}$, where $\mathrm{I} = \mathrm{m}_e \mathrm{r}^2$. The ring radius r can be approximated by the C=C distance in benzene, which is 1.39 Å, and m_e is the mass of an electron (9.109×10^{-31} kg). **(7 pts)**

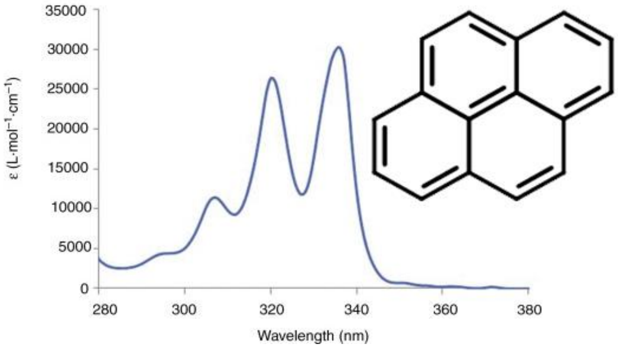



From Orndorff et al. J. Am. Chem. Soc., 1928, 50, 3, 831-837

Hint: to do these conversions I usually remember the following conversion factors:

$1\ \mathrm{J} = 6.242 \times 10^{18}$ eV and the wavelength in nanometers from eV is: $\mathrm{nm} = \frac{1240}{\mathrm{eV}}$ (i.e. divide 1240 by the energy in eV to get the the absorption in nanometers).

b. The absorption spectrum of pyrene is as shown here. It seems that the absorption is at ~340 nm. Can you calculate the radius of pyrene and show that it is greater than benzene (obviously)? **(7 pts)**



Problems: Theoretical or Explain in Words

1. *Did I mention that people who are good at math are really really rich?*

We will practice with differential equations of more than one variable. The purpose of this exercise is to convert the eigenvalue equation into a separable form composed of "mini-Schrodinger" differential equations that are solved separately. We will also see that the eigenvalue may become a part of only one of these mini-differential equations.

Let's say that we must solve the following differential equation called $\widehat{\mathrm{H}}$:

$$\widehat{\mathrm{H}} = \frac{1}{\mathrm{x}}\frac{\partial^2}{\partial \mathrm{y}^2} + \frac{1}{\mathrm{x}}\frac{\partial}{\partial \mathrm{x}}$$

a. Let's see if the equation is separable. To do first apply a solution ψ to the right: $\widehat{\mathrm{H}}\psi = \mathrm{E}\psi$, and then divide by the same on the left $\frac{1}{\psi}\widehat{\mathrm{H}}\psi = \frac{1}{\psi}\mathrm{E}\psi$. Since we assume $\psi = \psi(\mathrm{x})\psi(\mathrm{y})$ the result is:

$$\frac{1}{\psi(\mathrm{x})\psi(\mathrm{y})}\widehat{\mathrm{H}}\psi(\mathrm{x})\psi(\mathrm{y}) = \frac{1}{\psi(\mathrm{x})\psi(\mathrm{y})}\mathrm{E}\psi(\mathrm{x})\psi(\mathrm{y})$$

where E is the eigenvalue. Please do so as above and simplify whenever possible. ***Hint:*** here is an example of simplification: $\frac{1}{f(x)f(y)f(z)}\frac{\partial}{\partial \mathrm{x}}\frac{\partial}{\partial \mathrm{y}}f(x)f(y)f(z) = \frac{1}{f(x)f(y)}\frac{\partial}{\partial \mathrm{x}}f(x)\frac{\partial}{\partial \mathrm{y}}f(y)$ **(5 pts)**

b. Now to demonstrate separability you have to do some algebra on your answer from pt. a to make it look like:

$$\{terms\ with\ y\} + \{terms\ with\ x\} = 0$$

The problem with the above is that your answer form pt. a has this term: $\frac{1}{\psi(\mathrm{y})}\frac{1}{\mathrm{x}}\frac{\partial^2}{\partial \mathrm{y}^2}\psi(\mathrm{y})$, hence both "x" and "y" are in this same expression. This isn't allowed, please use some very simple algebra to remove "x" from this "y" term and tell us the result. Also, the eigenvalue "E" has now become part of one of the terms- which is it (the "x" or "y")?

(2 pts)

c. Suppose that you somehow know that $\psi(\mathrm{y}) = \mathrm{e}^{\mathrm{iq\cdot y}}$, where q is an integer. Please simplify the expression below by inserting $\psi(\mathrm{y}) = \mathrm{e}^{\mathrm{iq\cdot y}}$: **(3 pts)**

$$\frac{1}{\psi(\mathrm{y})}\frac{\partial^2}{\partial \mathrm{y}^2}\psi(\mathrm{y}) + \frac{1}{\psi(\mathrm{x})}\frac{\partial}{\partial \mathrm{x}}\psi(\mathrm{x}) - \mathrm{E}\cdot\mathrm{x} = 0$$

d. Now we often have to solve the mini-Schrodinger "x" equation by inserting values for q. Let's say that, if q=0 then $\psi(\mathrm{x}) = \mathrm{e}^{\mathrm{x}^2}$. Can you solve the equation from your answer to pt. c for the eigenvalue "E"? ***Hint***: E=2. **(5 pts)**

2. In 2-D, the Hamiltonian of the free wave (no potential energy) is:

$$\frac{-\hbar^2}{2\mathrm{m}}\left(\frac{\partial^2}{\partial \mathrm{x}^2} + \frac{\partial^2}{\partial \mathrm{y}^2}\right)$$

a. Show that writing the total wavefunction as: $\Psi(\mathrm{x},\mathrm{y}) = \Psi(\mathrm{x}) + \Psi(\mathrm{y})$ is incorrect because it is not an eigenfunction of the Hamiltonian, i.e.:

$$\widehat{\mathrm{H}}\Psi(\mathrm{x},\mathrm{y}) \neq \mathrm{E}\cdot\Psi(\mathrm{x},\mathrm{y})$$

where $\mathrm{E} = \mathrm{E_x} + \mathrm{E_y}$. You can assume that: $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\Psi(\mathrm{x}) = \mathrm{E_x}\cdot\Psi(\mathrm{x})$ and: $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{y}^2}\Psi(\mathrm{y}) = \mathrm{E_y}\cdot\Psi(\mathrm{y})$ and $\mathrm{E_x} \neq \mathrm{E_y}$. Of course $\frac{-\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial \mathrm{x}^2}\Psi(\mathrm{y}) = 0$, etc. **(5 pts)**

b. Now you can show that a proper wavefunction has the form:

$$\Psi(x,y) = \Psi(x) \cdot \Psi(y)$$

because then $\widehat{H}\Psi(x,y) = E \cdot \Psi(x,y)$ where $E = E_x + E_y$. **(5 pts)**

3. a. Let's say that we have an atom with bonds in both the x- and y-directions. The Hamiltonian is:

$$\frac{-\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right\} + \frac{1}{2}k_f x^2 + \frac{1}{2}k_f y^2$$

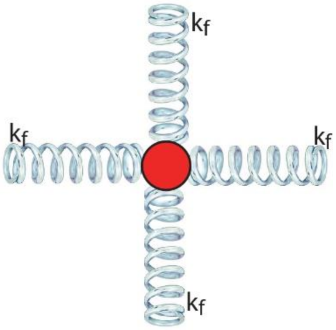
Given that the 1-D normalized ground state wavefunction is:

$$\Psi(x) = \left(\frac{1}{\pi\alpha}\right)^{\frac{1}{4}} e^{\frac{-x^2}{2\alpha^2}}$$

please use your instincts to write down what you think the 2D wavefunction is. Hint: You don't have to derive anything- you should be able to guess a proper wavefunction with the information provided. **(4 pts)**

b. I have taken a vibrational potential in the x-direction and added a y dimension. The y potential energy is flat but becomes infinite at y=0 and y=L as shown here. What do you expect the ground state wavefunction to be? ***Hint:*** You might have to look up one of the normalized wavefunctions we studied earlier.

(6 pts)



4. Here we will demonstrate that a 2D rigid rotor ("electron-on-a-string") can absorb light.

a. The 2D rigid rotor wavefunctions are: $\Psi = \frac{1}{\sqrt{2\pi}} e^{i \cdot m\phi}$. What is the angular momentum change going from the m=1 state to the m=2 state if the rigid rotor absorbs light? Hint, the angular momentum operator is $\hat{j}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$. **(5 pts)**

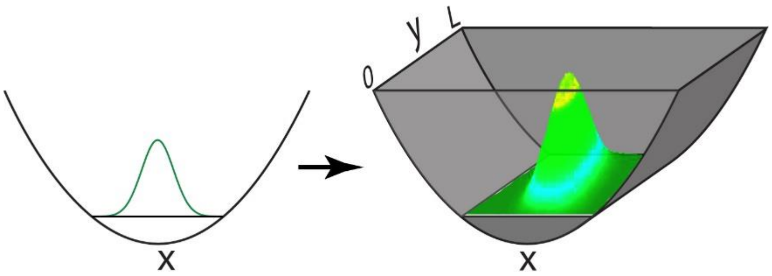
b. The angular momentum of light is $\hbar$, so do you think a 2D rigid rotor can absorb light? **(2 pts)**

Answer: a. First, calculate the angular momentum of each state. For the m=2:

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}\frac{1}{\sqrt{2\pi}}e^{i\cdot 2\phi} = \frac{\hbar}{i}2i \cdot \frac{1}{\sqrt{2\pi}}e^{i\cdot 2\phi} = 2\hbar\frac{1}{\sqrt{2\pi}}e^{i\cdot 2\phi}$$

Therefore the angular momentum of the m=2 state is $2\hbar$. Likewise the angular momentum of the m=1 state is evaluated from: $\frac{\hbar}{i}\frac{\partial}{\partial\phi}\frac{1}{\sqrt{2\pi}}e^{i\phi} = \frac{\hbar}{i}i \cdot \frac{1}{\sqrt{2\pi}}e^{i\phi} = \hbar\frac{1}{\sqrt{2\pi}}e^{i\phi}$, and is thus $\hbar$.

As a result, the gain in angular momentum is $2\hbar - \hbar = \hbar$.



b. The angular momentum of light is conserved by the transition of the rigid rotor so yes the 2D rigid rotor can absorb light.

5. Now that we are working in more than one dimension, you should know that the flux operator is actually:

$$\frac{1}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*)$$

The ∇ (del) operator in cylindrical coordinates is: $\nabla = \frac{\partial}{\partial \mathrm{r}} + \frac{1}{\mathrm{r}}\frac{\partial}{\partial \phi} + \frac{\partial}{\partial \mathrm{z}}$.

a. First simplify the flux operator given that the 2D rigid rotor is not moving in r or z. **(3 pts)**

b. So, what is the flux of the 2D rigid rotor given $\psi = e^{\mathrm{im}\cdot\phi}$? **(7 pts)**

6. The fact that the flux isn't 0 means that the 2D rigid rotor particle with $\psi = e^{i\cdot\phi}$ is moving, as in the previous problem. However, would the flux be for $\psi = e^{i\cdot\phi} + e^{-i\cdot\phi}$? This question is rather difficult, so we will break it down into parts.

a. Please evaluate $\psi^* \frac{\partial}{\partial\phi}\psi = (e^{-i\cdot\phi} + e^{i\cdot\phi})\frac{\partial}{\partial\phi}(e^{i\cdot\phi} + e^{-i\cdot\phi})$ **(5 pts)**

b. Next evaluate $\psi \frac{\partial}{\partial\phi}\psi^* = (e^{i\cdot\phi} + e^{-i\cdot\phi})\frac{\partial}{\partial\phi}(e^{-i\cdot\phi} + e^{i\cdot\phi})$ **(5 pts)**

c. Last, evaluate $\frac{1}{2\mathrm{mi}\cdot\mathrm{r}}\left(\psi^*\frac{\partial}{\partial\phi}\psi - \psi\frac{\partial}{\partial\phi}\psi^*\right) = \frac{1}{2\mathrm{mi}\cdot\mathrm{r}}(\mathrm{pt.\,a} - \mathrm{pt.\,b})$ **(2 pts)**

7. To solve the 3-D Hamiltonian you must show that the radial and angular wavefunctions are separable: $\Psi(\mathrm{r},\theta,\phi) = \Psi(\mathrm{r})\cdot\Psi(\theta)\cdot\Psi(\phi)$ which you do by demonstrating that the differential equation: $\frac{\partial^2}{\partial \mathrm{r}^2} + \frac{2}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}} + \frac{1}{\mathrm{r}^2}\left(\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right)$ can be separated into two smaller ones. What does that even mean? We will explain by first simplifying the equation above as:

$$\frac{\partial^2}{\partial \mathrm{r}^2} + \frac{2}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}} + \frac{1}{\mathrm{r}^2}\widehat{\Lambda}$$

where $\widehat{\Lambda}$ is an operator that has all the angles (θ,ϕ) in it. Next, we act on the wavefunction on the right and divide it out on the left like: $\frac{1}{\Psi}\cdot\widehat{\Theta}\cdot\Psi = \frac{1}{\Psi}\cdot \mathrm{E}\cdot\Psi = \mathrm{E}$

$$\frac{1}{\Psi(\mathrm{r})\cdot\Psi(\theta)\cdot\Psi(\phi)}\left(\frac{\partial^2}{\partial \mathrm{r}^2} + \frac{2}{\mathrm{r}}\frac{\partial}{\partial \mathrm{r}} + \frac{1}{\mathrm{r}^2}\widehat{\Lambda}\right)\cdot\Psi(\mathrm{r})\cdot\Psi(\theta)\cdot\Psi(\phi) = \mathrm{E}$$

a. Use the following notation: $\frac{\partial^2}{\partial \mathrm{r}^2}\Psi(\mathrm{r}) = \Psi''(\mathrm{r})$ and $\frac{\partial}{\partial \mathrm{r}}\Psi(\mathrm{r}) = \Psi'(\mathrm{r})$, show that the above can be simplified into:

$$\frac{\Psi''(\mathrm{r})}{\Psi(\mathrm{r})} + \frac{2\cdot\Psi'(\mathrm{r})}{\mathrm{r}\cdot\Psi(\mathrm{r})} + \frac{1}{\mathrm{r}^2\cdot\Psi(\theta)\cdot\Psi(\phi)}\widehat{\Lambda}\cdot\Psi(\theta)\cdot\Psi(\phi) = \mathrm{E}$$

Hint: This is easier than it looks- just look at the number of points for this question! **(6 pts)**

b. Now the equation above is **almost** separable, except that the 3rd term:

$$\frac{1}{\mathrm{r}^2\cdot\Psi(\theta)\cdot\Psi(\phi)}\widehat{\Lambda}\cdot\Psi(\theta)\cdot\Psi(\phi)$$

has both angles (θ,ϕ) and an $\frac{1}{\mathrm{r}^2}$ term in it. Can you show that the equation can be separated by multiplying by r^2 and do some algebra to yield:

$$\mathrm{r}^2\frac{\Psi''(\mathrm{r})}{\Psi(\mathrm{r})} + 2\mathrm{r}\frac{\Psi'(\mathrm{r})}{\Psi(\mathrm{r})} + \frac{1}{\Psi(\theta)\cdot\Psi(\phi)}\widehat{\Lambda}\cdot\Psi(\theta)\cdot\Psi(\phi) = \mathrm{E}\cdot\mathrm{r}^2$$

Hint: Like pt. a this is easier than it looks. **(4 pts)**

8. Time for some operator practice. Please show that, if you apply a 2p wavefunction:

$$\psi = \sin(\theta)\cdot e^{i\phi}$$

to the 3D rigid rotor Hamiltonian:

$$\frac{-\hbar^2}{2\mathrm{I}}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}\Psi = \mathrm{E}\cdot\Psi$$

we should derive:

$$\frac{\hbar^2}{2\mathrm{I}}l(l+1)\Psi = \frac{\hbar^2}{\mathrm{I}}\cdot\sin(\theta)\cdot e^{i\phi}$$

since $l = 1$ for a p state. Hence, the energy of this wavefunction is $\frac{\hbar^2}{\mathrm{I}}$. **(10 pts)**

Hint: Let's just leave the constants out of the derivation first, leaving you to solve:

$$\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\sin(\theta)\cdot e^{i\phi}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\cdot e^{i\phi}$$

Once you power through this you can multiply the results by $\frac{-\hbar^2}{2\mathrm{I}}$. Here is an identity you need: $\frac{(1-\cos^2(\theta))}{\sin(\theta)} = \sin(\theta)$.

9. Time for some operator practice. Please show that, if you apply a 2p wavefunction:

$$\psi = \sin(\theta)\cdot e^{-i\phi}$$

to the 3D rigid rotor Hamiltonian:

$$\frac{-\hbar^2}{2\mathrm{I}}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}\Psi = \mathrm{E}\cdot\Psi$$

you should derive an energy of:

$$\mathrm{E}\cdot\Psi = \frac{\hbar^2}{2\mathrm{I}}l(l+1)\cdot\Psi = \frac{\hbar^2}{\mathrm{I}}\cdot\sin(\theta)\cdot e^{-i\phi}$$

since $l = 1$ for a p state. Hence, the energy of this wavefunction is $\frac{\hbar^2}{\mathrm{I}}$. **(10 pts)**

Hint: Let's just leave the constants out of the derivation first, leaving you to solve:

$$\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\sin(\theta)\cdot e^{-i\phi}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\sin(\theta)\cdot e^{-i\phi}$$

Once you power through this you can multiply the results by $\frac{-\hbar^2}{2\mathrm{I}}$. Here is an identity you need: $\frac{(1-\cos^2(\theta))}{\sin(\theta)} = \sin(\theta)$.

10. a. 3D Integrals! The ground state angular wavefunction of the $2p_z$ orbital is:

$$\psi_{2p_z}(\theta,\phi) = \frac{\sqrt{3}}{2\sqrt{\pi}}\cos(\theta)$$

Can you integrate it to show that it is normalized: $\int_0^{2\pi}\int_0^{\pi}\left|\psi_{2p_z}(\theta,\phi)\right|^2\partial\theta\,\partial\phi = 1$? **(4 pts)**

Hint: it won't work.

b. The ground state angular wavefunction of the $2p_x$ orbital is:

$$\psi_{2p_x}(\theta,\phi) = \frac{\sqrt{3}}{2\sqrt{\pi}}\sin(\theta)\cos(\phi)$$

Can you integrate it to show that it is normalized: $\int_0^{2\pi}\int_0^{\pi}\left|\psi_{2p_x}(\theta,\phi)\right|^2\partial\theta\,\partial\phi = 1$? **(4 pts)**

Hint: it still won't work.

c. Now repeat your effort from pt. a to show that: $\int_0^{2\pi}\int_0^{\pi}\left|\psi_{2p_z}(\theta,\phi)\right|^2\mathbf{\sin(\theta)}\,\partial\theta\,\partial\phi$ **(5 pts)**

d. Now repeat your effort from pt. b to show that $\int_0^{2\pi}\int_0^{\pi}\left|\psi_{2p_x}(\theta,\phi)\right|^2\mathbf{\sin(\theta)}\,\partial\theta\,\partial\phi$ **(5 pts)**

11. a. 3D Integrals! The ground state 1s radial wavefunction of the hydrogen atom is:

$$\psi(r) = \frac{1}{\pi^{1/2}(a_0)^{3/2}} e^{-r/a_0}$$

Can you integrate the wavefunction to show that it is normalized, i.e. $\int_0^\infty |\psi(r)|^2 \, \partial r = 1$? ***Hint:*** it won't work.

(5 pts)

b. Try to repeat your effort from pt. a to show that $\int_0^\infty |\psi(r)|^2 \, \mathbf{4\pi r^2} \, \partial r = 1$ **(5 pts)**

12. Can you propose why, in questions 1 and 2, the addition of $4\pi r^2 \sin(\theta)$ resulted in the wavefunctions appearing to be properly normalized? **(5 pts)**

Answer: This factor is a Jacobian, and it is necessary to use it in 3D integrals.

13. In class it was discussed how the p_x and p_y orbitals come about from addition or subtraction of the m=±1 spherical harmonics. Now let's do the d-orbitals. Table 1 lists the spherical harmonic (3D rigid rotor wavefunctions). Can you fill out Table 2 with the proper descriptions of d-orbital states as well as identifying them?

Hint: $x = r \cdot \cos(\phi)\sin(\theta)$, $y = r \cdot \sin(\phi)\sin(\theta)$, and $z = r \cdot \cos(\theta)$.

Table 1:

$Y_{l=2,m=0}$	$3 \cdot \cos^2(\theta) - 1$
$Y_{l=2,m=1}$	$\cos(\theta) \cdot \sin(\theta) \cdot e^{i\phi}$
$Y_{l=2,m=-1}$	$\cos(\theta) \cdot \sin(\theta) \cdot e^{-i\phi}$
$Y_{l=2,m=2}$	$\sin^2(\theta) \cdot e^{2i\phi}$
$Y_{l=2,m=-2}$	$\sin^2(\theta) \cdot e^{-2i\phi}$

Table 2: **(8 pts)**

Ψ	result	d-function
$r^2 \times Y_{l=2,m=0}$	**a.**	**a.**
$r^2 \times (Y_{l=2,m=2} + Y_{l=2,m=-2})$	$r^2 \cdot \sin^2(\theta)\,(\cos^2(\phi) - \sin^2(\phi))$	x^2-y^2
$r^2 \times (Y_{l=2,m=2} - Y_{l=2,m=-2})$	**b.**	**b.**
$r^2 \times (Y_{l=2,m=1} + Y_{l=2,m=-1})$	**c.**	**c.**
$r^2 \times (Y_{l=2,m=1} - Y_{l=2,m=-1})$	**d.**	**d.**

Double Hint: $\sin(2x) = 2\sin(x)\cos(x)$.

Chapter 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:

$$\frac{1}{\lambda} = \mathrm{R}\left(\frac{1}{\mathrm{n}_1^2} - \frac{1}{\mathrm{n}_2^2}\right)$$

where λ is the emission wavelength, n_1 and n_2 are whole numbers, and $\mathrm{R} = 1.097 \times 10^7\ \mathrm{m}^{-1}$ 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

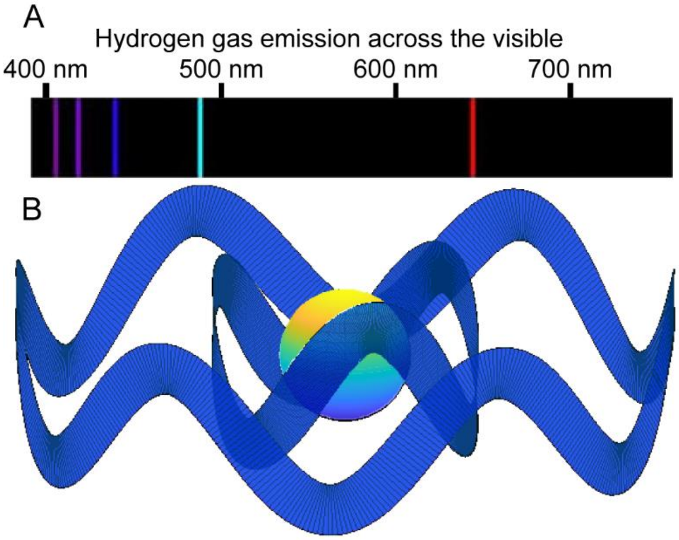


Figure 15.1. A. The emission spectrum of hydrogen gas reveals discrete lines as described by Balmer's formula. **B.** Early descriptions of the hydrogen atom incuded circulating electrons (Bohr) or wave-like electrons (Schrodinger).

reveals another aspect of science, which is that a scientific theory is either everything or it is nothing.

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 ($\mathrm{mv} \cdot \mathrm{r}$) was assumed to take integer values of $\hbar$, which is the reduced Planck constant (h/2π):

$$\mathrm{mv} \cdot \mathrm{r} = \mathrm{n} \cdot \hbar$$

where n=1, 2, 3, etc. This means that velocity must be quantized: $\mathrm{v} = \frac{\mathrm{n}\hbar}{\mathrm{m} \cdot \mathrm{r}}$. Next, Bohr conjectured that the "outward" centripetal force: $\frac{\mathrm{mv}^2}{\mathrm{r}}$ matches the "inward" Coulomb attraction force:

$$\frac{\mathrm{mv}^2}{\mathrm{r}} = \frac{\mathrm{e}^2}{4\pi\varepsilon_0 \mathrm{r}^2}$$

According to the above $\mathrm{v} = \sqrt{\frac{\mathrm{e}^2}{4\pi\varepsilon_0 \cdot \mathrm{m} \cdot \mathrm{r}}}$, which must be equal to our previous expression velocity:

$$\frac{\mathrm{n}\hbar}{\mathrm{m} \cdot \mathrm{r}} = \sqrt{\frac{\mathrm{e}^2}{4\pi\varepsilon_0 \cdot \mathrm{m} \cdot \mathrm{r}}}$$

This allows us to solve for the electron's radius: $\mathrm{r} = \frac{4\pi\varepsilon_0 \cdot \mathrm{n}^2 \hbar^2}{\mathrm{m} \cdot \mathrm{e}^2}$, which is a function of the integer n. If n = 1 the radius is: $\mathrm{r} = \frac{4\pi\varepsilon_0 \hbar^2}{\mathrm{m} \cdot \mathrm{e}^2}$, which is the famous Bohr unit of length $a_0 = 0.053\times10^{-9}$ m.

The energy can be calculated by adding the kinetic and potential from the electrostatic attraction: $\frac{1}{2}\mathrm{mv}^2 - \frac{\mathrm{e}^2}{4\pi\varepsilon_0 \mathrm{r}}$, 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:

$$\mathrm{E} = -\frac{\mathrm{e}^4 \mathrm{m}}{32\pi^2\varepsilon_0^2 \cdot \hbar^2} \cdot \frac{1}{\mathrm{n}^2}$$

Inserting n = 1 gives the ground state energy: $-\frac{\mathrm{m} \cdot \mathrm{e}^4}{32\pi^2\varepsilon_0^2 \cdot \hbar^2} = -13.6$ 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: $\psi_{\mathrm{total}} = \psi_1\psi_2$, 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:

$$\psi_{\mathrm{total}} \approx \psi_{\mathrm{electron}} \cdot \psi_{\mathrm{proton}}$$

Since the proton is ~1800× 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 ~1836× 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 $\hat{\phi}$ 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:

$$\frac{-\hbar^2}{2\mu}\left(\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\frac{1}{r^2}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}\right)\psi(r,\theta,\phi)-\frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi)$$
$$=E\cdot\psi(r,\theta,\phi)$$

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 $\frac{-2\mu}{\hbar^2}r^2$:

$$\left(r^2\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}\right)\psi(r,\theta,\phi)+\frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2\psi(r,\theta,\phi)$$
$$=-\frac{2\mu}{\hbar^2}r^2\cdot E\cdot\psi(r,\theta,\phi)$$

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: $\frac{1}{R(r)Y(\theta,\phi)}\hat{H}R(r)Y(\theta,\phi)$:

$$\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r)+\frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2+\frac{1}{Y(\theta,\phi)}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}Y(\theta,\phi)$$

$$=-\frac{2\mu}{\hbar^2}r^2E$$

Now we group all the r terms on one side and the angular θ and ϕ on the other:

$$\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r)+\frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2+\frac{2\mu}{\hbar^2}r^2E$$

$$=\frac{1}{Y(\theta,\phi)}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}Y(\theta,\phi)$$

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

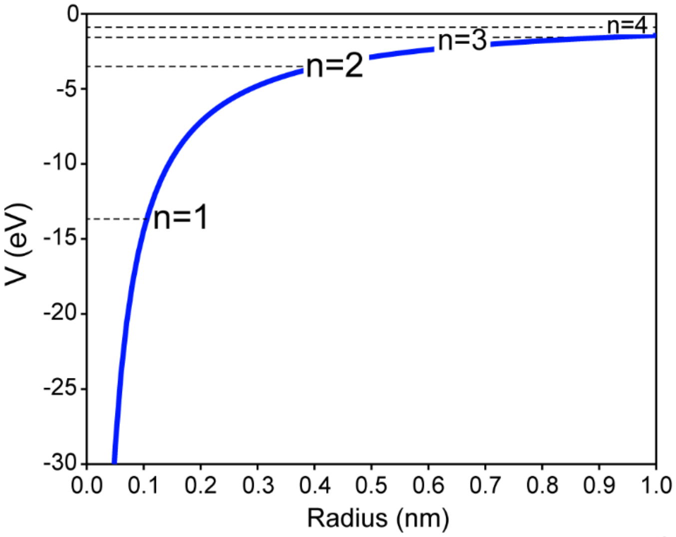


Figure 15.2. The hydrogen atom's Coulomb potential and eigenvalues of the n=1,2,3 and 4 states. An electron at an infinite distance from the nucleus has an energy of 0 eV.

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 $\mathrm{R(r)} \rightarrow 0$ as $\mathrm{r} \rightarrow \infty$. 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 $l = 0, 1, 2 \ldots (\mathrm{n} - 1)$ 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 $\mathrm{m}_l = -l \ldots 0 \ldots l$ 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 wavefunctions that we know as $\mathrm{p_x}$, $\mathrm{p_y}$ and $\mathrm{p_z}$. 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.

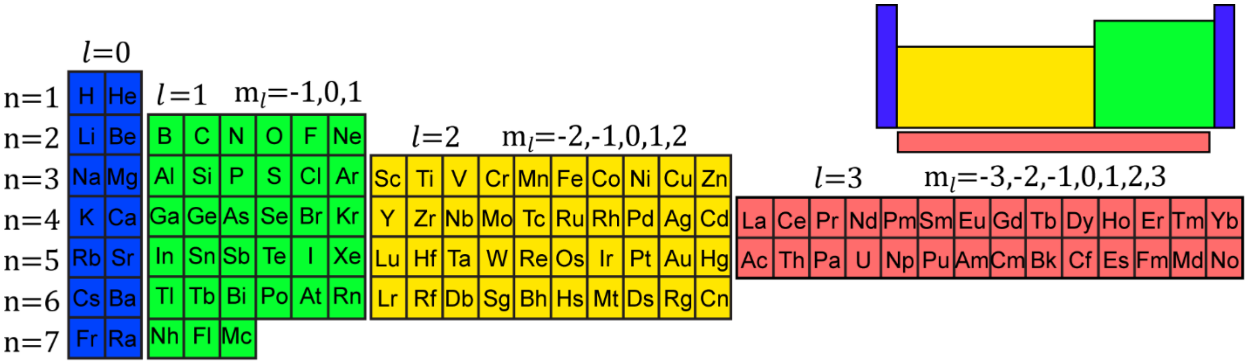


Figure 15.3. The periodic table of elements as arranged by l quantum number. The reason that the various blocks have 2, 6, 10 and 14 colums is due to the m_l quantum number. Inset shows the traditional arrangement of the periodic table which is the result of shielding.

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

n	l	m	$\mathrm{R}_{\mathrm{n},l}(\mathrm{r})$	$\mathrm{Y}_{l,\mathrm{m}}(\theta,\phi)$
1s	0		$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2\pi}}$
2s	0		$\frac{1}{2\sqrt{2}(a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2\pi}}$
3s	0		$\frac{2}{81\sqrt{3}(a_0)^{3/2}}\left(27-\frac{18r}{a_0}+\frac{2r^2}{a_0^2}\right)e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2\pi}}$
2p	1	m=0	$\frac{1}{2\sqrt{6}(a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{\sqrt{6}}{2}\cos(\theta)\frac{1}{\sqrt{2\pi}}$
		m=±1	$\frac{1}{2\sqrt{6}(a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{\sqrt{3}}{2}\sin(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3p	1	m=0	$\frac{4}{81\sqrt{6}(a_0)^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{\sqrt{6}}{2}\cos(\theta)\frac{1}{\sqrt{2\pi}}$
		m=±1	$\frac{1}{81\sqrt{6}(a_0)^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{\sqrt{3}}{2}\sin(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3d	2	m=0	$\frac{4}{81\sqrt{30}(a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{10}}{4}(3\cos^2(\theta)-1)\frac{1}{\sqrt{2\pi}}$
		m=±1	$\frac{4}{81\sqrt{30}(a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{15}}{2}\sin(\theta)\cos(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
		m=±2	$\frac{4}{81\sqrt{30}(a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{15}}{4}\sin^2(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i2\phi}$

Table 15.1 Hydrogen atom radial and angular wavefunctions.

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:

$$\frac{\partial^2}{\partial r^2} r \cdot R(r) - \frac{l(l+1)}{r} R(r) = 0$$

Example Problem 15.1

Problem: Can you show that the eigenvalue equation can be used to calculate the energy of the hydrogen atom 1s ground state using the radial wavefunction $R_{1,0}(r) = 2(a_0)^{-3/2}\cdot e^{-r/a_0}$?

Answer: The Hamiltonian for the 1s is simplified as $l = 0$ and there is no rotational kinetic energy:

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}\cdot r\cdot 2(a_0)^{-3/2}\cdot e^{-r/a_0}+\frac{-e^2}{4\pi\varepsilon_0 r}\cdot r\cdot 2(a_0)^{-3/2}\cdot e^{-r/a_0}=$$

$$\frac{-2\hbar^2}{2\mu\cdot(a_0)^{3/2}}\cdot\frac{\partial^2}{\partial r^2}\left(r\cdot e^{-r/a_0}\right)+\frac{-2}{(a_0)^{3/2}}\frac{e^2}{4\pi\varepsilon_0}e^{-r/a_0}=$$

$$\frac{-\hbar^2}{\mu\cdot(a_0)^{3/2}}\frac{\partial}{\partial r}\left(e^{-r/a_0}-\frac{1}{a_0}\cdot r\cdot e^{-r/a_0}\right)+\frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0}e^{-r/a_0}=$$

$$\frac{-\hbar^2}{\mu\cdot(a_0)^{3/2}}\left(-\frac{e^{-r/a_0}}{a_0}-\frac{e^{-r/a_0}}{a_0}+\frac{1}{a_0^2}\cdot r\cdot e^{-r/a_0}\right)+\frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0}e^{-r/a_0}=$$

$$\frac{2\hbar^2}{\mu\cdot(a_0)^{5/2}}e^{-r/a_0}-\frac{\hbar^2}{\mu\cdot(a_0)^{7/2}}\cdot r\cdot e^{-r/a_0}+\frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0}e^{-r/a_0}$$

Given $a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu\cdot e^2}$, simple rearrangement reveals: $\frac{e^2}{2\pi\varepsilon_0}=\frac{2\hbar^2}{\mu\cdot a_0}$ and thus $\frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0}=\frac{-1}{(a_0)^{3/2}}\frac{2\hbar^2}{\mu\cdot a_0}=\frac{-2\hbar^2}{\mu\cdot(a_0)^{5/2}}$. As a result, the 1st and 3rd term of the expression above cancel leaving:

$$-\frac{\hbar^2}{\mu\cdot(a_0)^{7/2}}\cdot r\cdot e^{-r/a_0}=-\frac{\hbar^2}{2\mu\cdot a_0^2}\cdot r\cdot 2(a_0)^{-3/2}\cdot e^{-r/a_0}=E\cdot r\cdot 2(a_0)^{-3/2}\cdot e^{-r/a_0}$$

Thus the energy is $E=-\frac{\hbar^2}{2\mu\cdot a_0^2}$. Inserting $a_0=\frac{4\pi\varepsilon_0\hbar^2}{\mu\cdot e^2}$ reveals $E=-\frac{\mu\cdot e^4}{32\pi^2\varepsilon_0^2\hbar^2}$, exactly as derived by Bohr and Schrödinger.

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 $R(r)\approx r^l\rightarrow 0$ prevents this from happening.

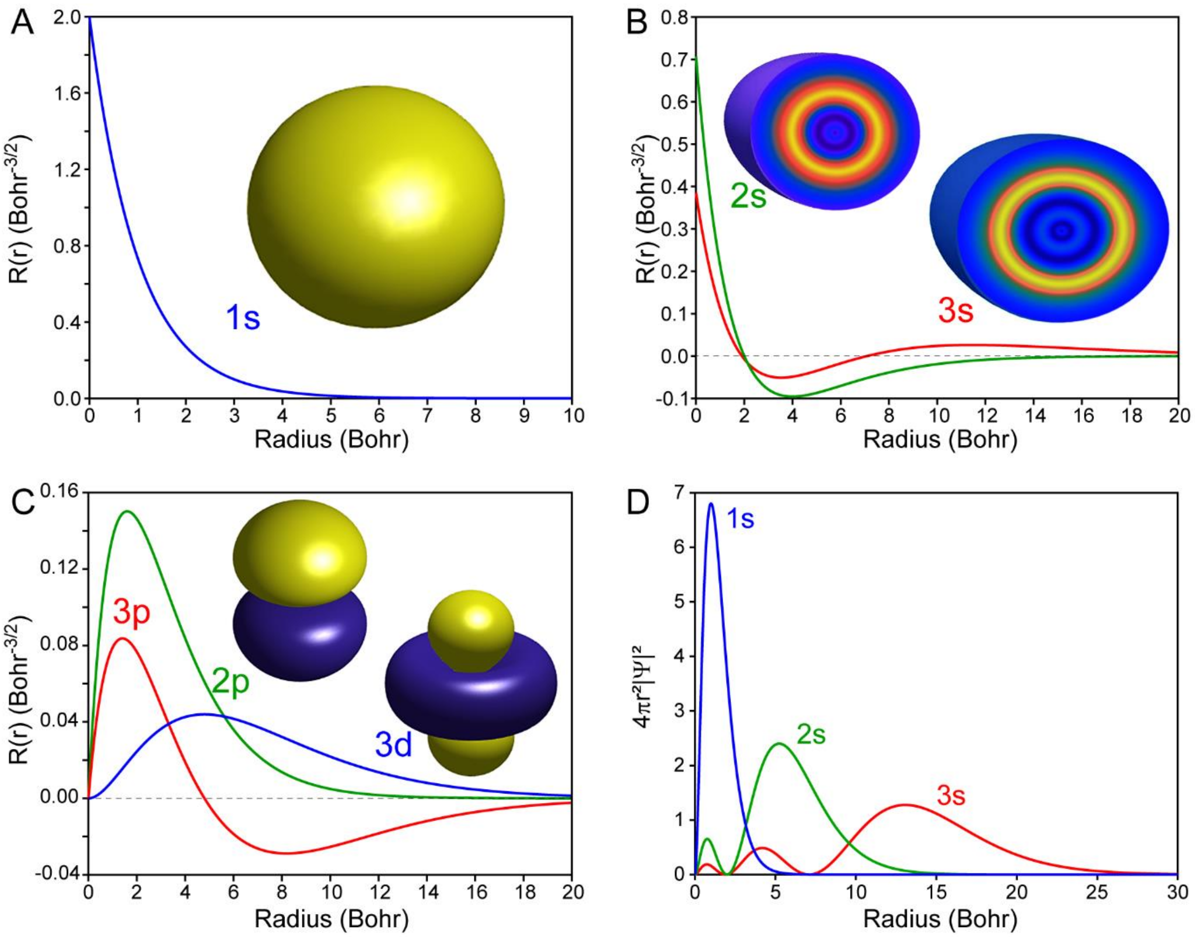


Figure 15.4. Radial wavefunctions for (A) the 1S state, (B) the 2S and 2P staes where the complex raidal nodes are observed in the solid rendering, (C) the 2P, 3P and 3D states. The $2P_Z$ and $3D_{Z^2}$ states are shown in space filling models. D. Radial distribution functions for hydrogenic 1s, 2s and 3s states.

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

Example Problem 15.2

Problem: Can you show that the average distance of the s-state electron from the nucleus increases with principal quantum number from n=1 to n=2?

Answer: While it is tempting to calculate $\langle r\rangle$ by integrating the radial wavefunction as

$$\langle r\rangle = \int_0^\infty R_{1,0}^*(r)\cdot r\cdot R_{1,0}(r)\,\partial r$$

this is a mistake since the normalization condition includes the angular wavefunctions and the volume-normalizing Jacobian factor. We should always double check that our wavefunctions are normalized, and we do so here for the $R_{1,0}(r)Y_{0,0}(\theta,\phi)$ from Table 15.1:

$$\int_0^\infty \left(2a_0^{-\frac{3}{2}}\cdot e^{-r/a_0}\right)^* \left(2a_0^{-\frac{3}{2}}\cdot e^{-r/a_0}\right) r^2\cdot\partial r = \frac{4}{a_0^3}\int_0^\infty e^{-2r/a_0}\cdot r^2\cdot\partial r$$

Using an integral identity reveals that the result is 1.0, which means the wavefunction is properly normalized and we may perform further calculations. For the 1s state:

$$\langle r\rangle = \int_0^\infty r^2\cdot r\cdot\left(2a_0^{-\frac{3}{2}}\cdot e^{-r/a_0}\right)^2 \partial r = \frac{3}{2}a_0$$

while the average distance for the 2s state is:

$$\langle r\rangle = \int_0^\infty r^2\cdot r\cdot\left(\frac{1}{2\sqrt{2}(a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\right)^2 \partial r = 6a_0$$

These results reveal that there is a significant increase in the average radial distance for electrons as a function of shell number as seen in Figure 15.4.

(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 $R_{1,0}(r) = N\cdot e^{-r/a_0}$ 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 $R_{n,l}^2$ 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 $\sim e^{-r/n \cdot a_0}$ 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 $r \to 0$ 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 $-\mathrm{m}_l$ (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 $\mathrm{m}_l = -1, 0, 1$ sub-states. Since the $\mathrm{m}_l = 1$ and $\mathrm{m}_l = -1$ have opposing magnetic fields, an external field will interact to split their energies while the $\mathrm{m}_l = 0$ 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.

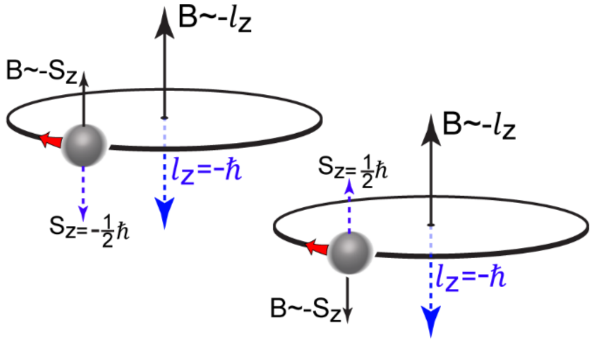


Figure 15.5. Spin orbit coupling affects the energy of l>0 states due to alignment of the orbital and spin magentic (B) fields.

The Hamiltonian for this interaction can be derived from the Einstein’s theory of relativity:

$$\hat{\mathrm{H}}_{\mathrm{SO}} = -\frac{\mu_{\mathrm{B}}}{\hbar \mathrm{m_e} \mathrm{e} \mathrm{c}^2}\frac{1}{\mathrm{r}}\frac{\partial \hat{\mathrm{V}}}{\partial \mathrm{r}}\hat{\mathrm{L}} \cdot \hat{\mathrm{S}}$$

where $\mu_{\mathrm{B}} = 9.274\ \mathrm{J} \cdot \mathrm{T}^{-1}$ 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 $\hat{\mathrm{H}}_{\mathrm{SO}} \sim \mathrm{A} \cdot \hat{\mathrm{L}} \cdot \hat{\mathrm{S}}$. The dot product of the two operators is defined as any standard vector: $\hat{\mathrm{L}} \cdot \hat{\mathrm{S}} = \hat{l}_{\mathrm{x}} \cdot \hat{\mathrm{s}}_{\mathrm{x}} + \hat{l}_{\mathrm{y}} \cdot \hat{\mathrm{s}}_{\mathrm{y}} + \hat{l}_{\mathrm{z}} \cdot \hat{\mathrm{s}}_{\mathrm{z}}$. 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 $\hat{\mathrm{J}}$ operator, where $\hat{\mathrm{J}} = \hat{\mathrm{L}} + \hat{\mathrm{S}}$. We encountered the issue of addition of angular momentum in Ch. 14, so you might want to review that section. Regardless, the operator $\hat{\mathrm{J}}^2$ contains the $\hat{\mathrm{L}} \cdot \hat{\mathrm{S}}$ dot product:

$$\hat{\mathrm{J}}^2 = \left(\hat{\mathrm{L}} + \hat{\mathrm{S}}\right)^2 = \hat{\mathrm{L}}^2 + \hat{\mathrm{S}}^2 + 2\hat{\mathrm{L}} \cdot \hat{\mathrm{S}}$$

We can rearrange the above to show that: $\hat{\mathrm{L}} \cdot \hat{\mathrm{S}} = \frac{1}{2}\left\{\hat{\mathrm{J}}^2 - \hat{\mathrm{L}}^2 - \hat{\mathrm{S}}^2\right\}$, where the $\hat{\mathrm{J}}$, $\hat{\mathrm{L}}$, and $\hat{\mathrm{S}}$ operators return their respective quantum numbers (j, l and s) such that the interaction is:

$$\mathrm{E}_{\mathrm{SO}} = \frac{\mathrm{A}}{2} \cdot \{j(j+1) - l(l+1) - s(s+1)\}$$

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 $2\mathrm{p}^1$ electron configuration, i.e. $l = 1$ and $\mathrm{s} = \frac{1}{2}$. As discussed in Ch. 14 the l and s angular momenta add to produce two possible j states:

$$\mathrm{j} = |l + \mathrm{s}| = \frac{3}{2} \quad \text{or} \quad \mathrm{j} = |l - \mathrm{s}| = \frac{1}{2}$$

Term symbols ($^{2S+1}\mathrm{L}_{\mathrm{j}}$) distinguish between the two as having $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$ electronic configurations. Spin-orbit coupling raises the energy of the $^2\mathrm{P}_{3/2}$ state:

$$\mathrm{E}_{\mathrm{SO}} = \mathrm{A} \cdot \left\{\frac{3}{2}\left(\frac{3}{2}+1\right) - 1(1+1) + \frac{1}{2}\left(\frac{1}{2}+1\right)\right\} = \frac{\mathrm{A}}{2} \cdot \left\{\frac{15}{4} - \frac{8}{4} - \frac{3}{4}\right\} = \frac{\mathrm{A}}{2}$$

while the $^2\mathrm{P}_{1/2}$ state is pushed downhill:

$$\mathrm{E}_{\mathrm{SO}} = \mathrm{A} \cdot \left\{\frac{1}{2}\left(\frac{1}{2}+1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right\} = \frac{\mathrm{A}}{2} \cdot \left\{\frac{3}{4} - \frac{8}{4} - \frac{3}{4}\right\} = -\mathrm{A}$$

Consequently the otherwise degenerate $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$ configurations are split as shown in Figure 15.6. Also shown is how the spin-orbit effect is observed from the H_{α} 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: $\frac{\partial \hat{\mathrm{V}}}{\partial \mathrm{r}}$, 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

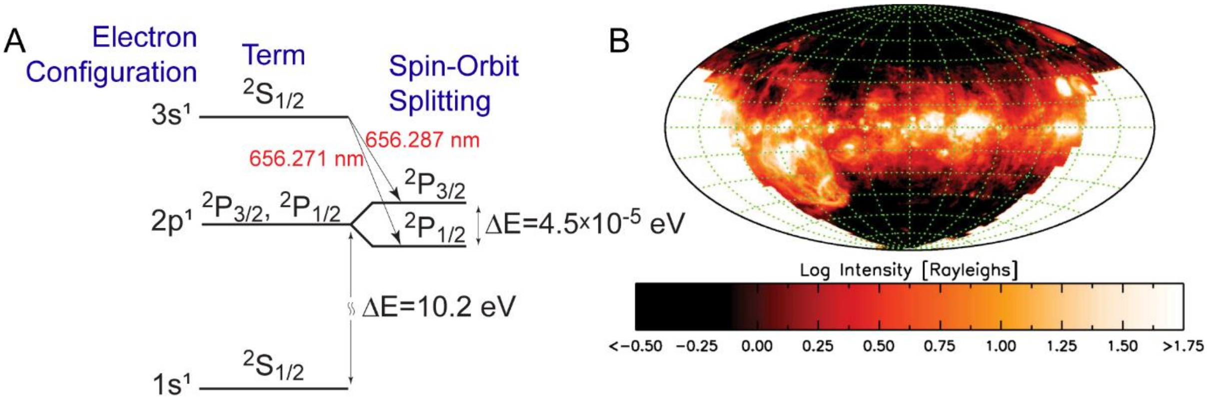


Figure 15.6 A. Energy levels for the hydrogen atom reveal splitting of the 2p state due to the spin-orbit effect. Emission from an excited 3s to 2p state results in red wavelength fluorescence called the hydrogen Hα line. **B.** Image of the Milkey Way galaxy taken at the Hα wavelength (1).

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 $\vec{\mu} = q_1 q_2 \vec{r}$. Here, q_1 and q_2 are the charges (for hydrogen, and electron and proton) and $\vec{r}$ is the distance between. The quantum mechanical analog is the dipole operator, which for the hydrogen atom is:

$$\hat{\mu} = -e^2 \cdot \hat{r}$$

We can calculate the expectation value of the dipole operator as it applied to a transition across energy states:

$$\langle\hat{\mu}\rangle = -e\cdot\langle\psi_f|\hat{r}|\psi_i\rangle = \int\int\int \psi_f^*(r,\theta,\phi)\cdot r\cdot\psi_i(r,\theta,\phi)\cdot\partial r\cdot\sin(\theta)\,\partial\theta\cdot\partial\phi$$

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 $\langle\hat{\mu}\rangle$, sometimes called the difference dipole moment, is related to the strength of the absorption. A large $\langle\hat{\mu}\rangle$ 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, $\langle\hat{\mu}\rangle$ tells us whether absorption of light occurs or not. If $\langle\hat{\mu}\rangle = 0$ then we say that the excited state is "optically silent". Otherwise, $\langle\hat{\mu}\rangle > 0$ 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 $\langle\hat{\mu}\rangle$; 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:

$$\hat{\mu} = -e^2\cdot\hat{x}$$

Since atoms are round and we are working in spherical coordinates, we have to substitute the x coordinate in the spherical

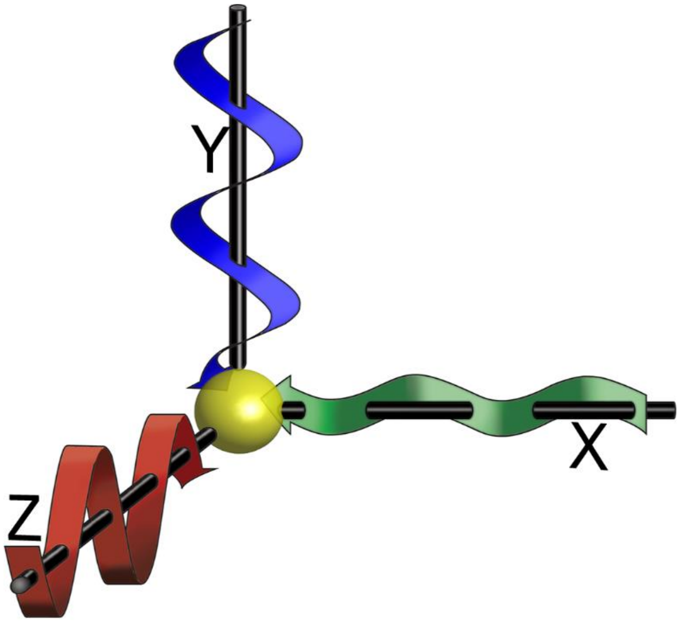


Figure 15.7. Different polarizations of light striking a ground state hydrogen atom results in angular dependence to the transition dipole moment.

form as: $\hat{\mu} = -e^2 \cdot r \cdot \sin(\theta)\cos(\phi)$. Inserting this into the expression for calculating difference dipole moment yields:

$$\langle\hat{\mu}\rangle = \int_0^\infty \psi_f^*(r) \cdot r \cdot \psi_i(r) \cdot 4\pi r^2\, \partial r \cdot \int_0^\pi \psi_f^*(\theta)\psi_i(\theta) \cdot \sin^2(\theta) \cdot \partial\theta \cdot \int_0^{2\pi} \psi_f^*(\phi)\psi_i(\phi) \cdot \cos(\phi) \cdot \partial\phi$$

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 $\langle\hat{\mu}\rangle \neq 0$ *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:

$$\widehat{H}(1,2) = \frac{-\hbar^2}{2\mu r^2}\nabla_1 + \frac{-\hbar^2}{2\mu r^2}\nabla_2 - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|}$$

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:

$$\psi_{\text{total}}(1,2) = \psi_1(1)\psi_2(2)$$

where the “(1)” and “(2)” are labels for the first and second electron and the subscripts on $\psi_{\mathbf{1}}$ and $\psi_{\mathbf{2}}$ 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 $\psi_{1S}(1)\psi_{1S}(2)$.

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 $\psi_{\text{total}}(1,2) \approx \psi_1(1)\psi_2(2)$ 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:

$$\int \psi^* \hat{H}\psi > E_{\text{exact}}$$

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: $\psi_{\mathrm{total}}(1,2) \approx \psi_{1S}(1)\psi_{1S}(2)$, 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:

$$\psi_{1,0}(\mathrm{r},\mathrm{Z}) = 2\left(\frac{\mathrm{Z}}{\mathrm{a_0}}\right)^{\frac{3}{2}} \mathrm{e}^{-\mathrm{Z}\cdot\mathrm{r}/\mathrm{a_0}}$$

(recall that Z = +1 for hydrogen). Next, we insert this function for electrons 1 and 2 and apply it to calculate the $\langle \mathrm{E} \rangle$ 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 $\langle \mathrm{E} \rangle$ by applying standard calculus definition of the minimum of a function:

$$\frac{\partial}{\partial \mathrm{Z}} \int \psi_{1S}(1)^{*}\psi_{1S}(2)^{*}\hat{\mathrm{H}}\psi_{1S}(1)\psi_{1S}(2) = 0 \; @ \; \mathrm{Z_{opt}}$$

While Z = +2 for helium, applying the above method we find that $\mathrm{Z_{opt}}$= +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: $\int_0^{a_0} R_{4s}^* \cdot R_{4s}(r) \cdot r^2\,\partial r =$

$$\frac{1}{96^2 \cdot {a_0}^3}\int_0^{a_0}\left\{\left(24 - 18\frac{r}{a_0} + 3\frac{r^2}{a_0^2} - \frac{r^3}{8 \cdot a_0^3}\right) \cdot e^{-r/4a_0}\right\}^2 \cdot r^2\,\partial r = 4.1 \times 10^{-3}$$

When we perform the same calculation using the 3d radial wavefunction we find:

$$\int_0^{a_0} {\Psi_{3d}}^* \cdot \Psi_{3d} \cdot r^2\,\partial r = 6.5 \times 10^{-6}$$

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

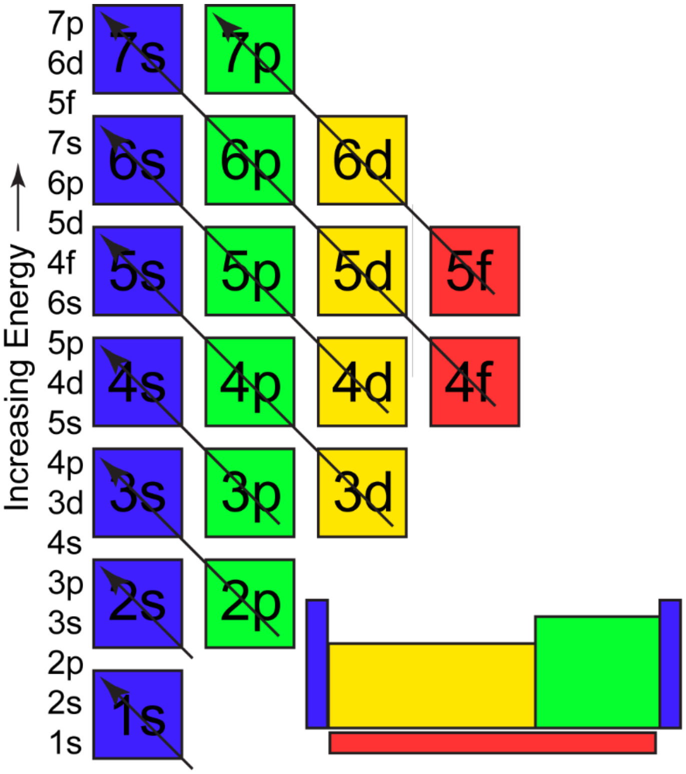


Figure 15.8. Shielding in multielectron atoms results in a reorganizational of atomic energy levels. This in turn affects the overall structure of the periodic table.

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 6th and 7th 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 $\psi_{\mathrm{spin}} = \alpha$ (the "up" ↑ state) and $\psi_{\mathrm{spin}} = \beta$ (the "down" ↓ state). The $\hat{S}_z$ operator acts upon them as:

$$\hat{S}_z\alpha = s_z \cdot \alpha = ½\hbar \cdot \alpha \quad \text{and} \quad \hat{S}_z \cdot \beta = s_z \cdot \beta = -½\hbar \cdot \beta$$

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:

$$\int \alpha^*\alpha = \int \beta^*\beta = 1 \quad \text{and} \quad \int \alpha^*\beta = \int \beta^*\alpha = 0$$

Electrons are assigned spin wavefunctions by labeling them as such; for example, $\psi_{\mathrm{spin}} = \alpha(1)\beta(2)$ 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: $\uparrow\uparrow = \alpha(1)\alpha(2)$. Rather they must have opposite s_z as: $\uparrow\downarrow = \alpha(1)\beta(2)$. 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:

$$\psi(1,2) = \psi_{\mathrm{space}}(1,2)\psi_{\mathrm{spin}}(1,2) = \psi_{1S}(1)\alpha(1) \cdot \psi_{1S}(2)\beta(2)$$

However, this approach easily allows us to create a wavefunction for a $1s^2$ ↑↑ configuration that violates the Pauli principle: $\psi_{1S}(1)\alpha(1) \cdot \psi_{1S}(2)\alpha(2)$. 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:

$$\psi_{\mathrm{total}}(1,2) = \psi_{\mathrm{space}}(1,2) \cdot \psi_{\mathrm{spin}}(1,2)$$

We create the inversion to interchange property within the spin manifold as:

$$\psi_{\mathrm{spin}}(1,2) = \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

To verify, we exchange the electron’s labels to find:

$$\alpha(2)\beta(1) - \alpha(1)\beta(2) = -\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

This is antisymmetry property we are looking for. The total singlet ground state wavefunction with space and spin is therefore:

$${}^1\Psi(1,2) = \psi_{\mathrm{space}}\psi_{\mathrm{spin}} \approx \psi_1(1)\psi_2(2)\left\{\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right\}$$

where the $\frac{1}{\sqrt{2}}$ is a normalization factor. It is now evident how the creation of an “illegal” $1s^2$ ↑↑ 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:

$${}^1\Psi(1,2) = \left\{\frac{\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)}{\sqrt{2}}\right\}\left\{\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right\}$$

This works because electron 1 can be in either the first or second spatial orbital, and the same is true for the 2nd 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:

$$\psi_{\text{spin}} = \alpha(1)\alpha(2) \qquad \psi_{\text{spin}} = \beta(1)\beta(2) \qquad \psi_{\text{spin}} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}$$

The above are symmetric with respect to interchange of the electron's labels, we must impart antisymmetry to the spatial wavefunctions as follows:

$$^3\Psi(1,2) = \left\{\frac{\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)}{\sqrt{2}}\right\}\left\{\begin{matrix} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\} \end{matrix}\right\}$$

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:

$$^3\Psi = \det\frac{1}{\sqrt{2}}\begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(2)\alpha(2) \\ \Psi_{2s}(1)\alpha(1) & \Psi_{2s}(2)\alpha(2) \end{vmatrix}$$

Expanding the determinant reveals:

$$^3\Psi = \frac{1}{\sqrt{2}}\{\Psi_{1s}(1)\alpha(1)\Psi_{2s}(2)\alpha(2) - \Psi_{2s}(1)\alpha(1)\Psi_{1s}(2)\alpha(2)\}$$

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:

$$^1\Psi = det\frac{1}{2}\left(\begin{vmatrix}\Psi_{1s}(1)\alpha(1) & \Psi_{1s}(2)\alpha(2)\\ \Psi_{1s}(1)\beta(1) & \Psi_{1s}(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\Psi_{1s}(1)\beta(1) & \Psi_{1s}(2)\beta(2)\\ \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(2)\alpha(2)\end{vmatrix}\right)$$

Simplification yields:

$$\frac{1}{2}\{\Psi_{1s}(1)\Psi_{1s}(2)+\Psi_{1s}(1)\Psi_{1s}(2)\}\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}$$

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:

$$\Psi = \det\frac{1}{\sqrt{3}}\begin{vmatrix}\Psi_{1s}(r_1)\alpha(1) & \Psi_{1s}(r_2)\alpha(2) & \Psi_{1s}(r_3)\alpha(3)\\ \Psi_{1s}(r_1)\alpha(1) & \Psi_{1s}(r_2)\alpha(2) & \Psi_{1s}(r_3)\alpha(3)\\ \Psi_{2s}(r_1)\alpha(1) & \Psi_{2s}(r_2)\alpha(2) & \Psi_{2s}(r_3)\alpha(3)\end{vmatrix}$$

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:

$$\int \Psi^1(1,2)^*\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^1(1,2)\cdot\partial\tau \quad \int \Psi^3(1,2)^*\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^3(1,2)\cdot\partial\tau$$

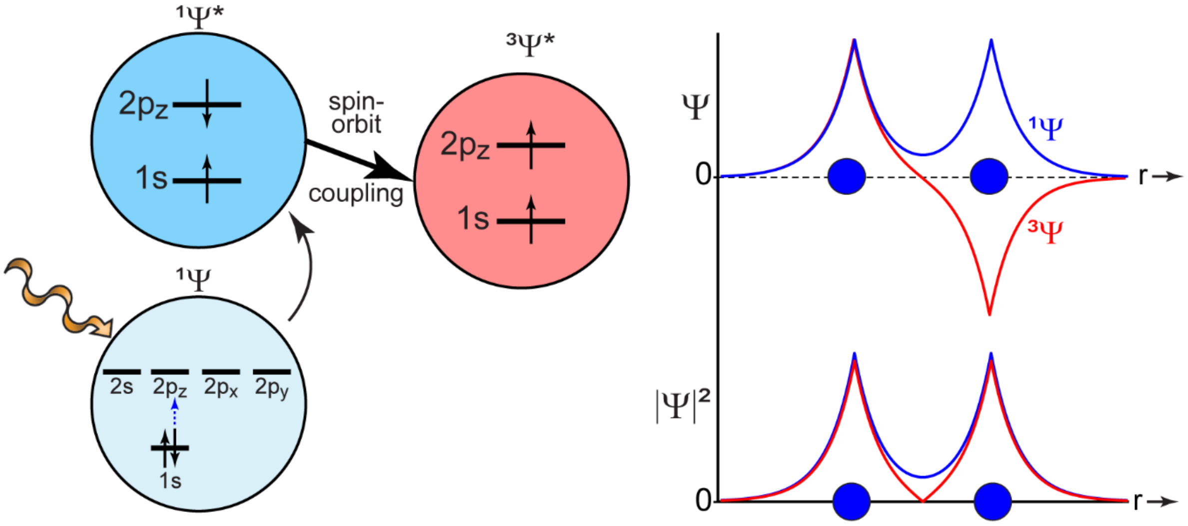


Figure 15.9. A. Excitation of the He atom creates an exicted singlet state due to the spin selection rule. Spin-orbit coupling allows for intersystem crossing into the lower energy triplet. **B.** Triplet states are lower in energy because of their antisymmetric space wavefunctions prevent electrons from crowding too close together as observed in singlet states.

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, $|\psi_1(1)|^2$, electrostatically interacting with the same for the second electron $|\psi_2(2)|^2$. 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

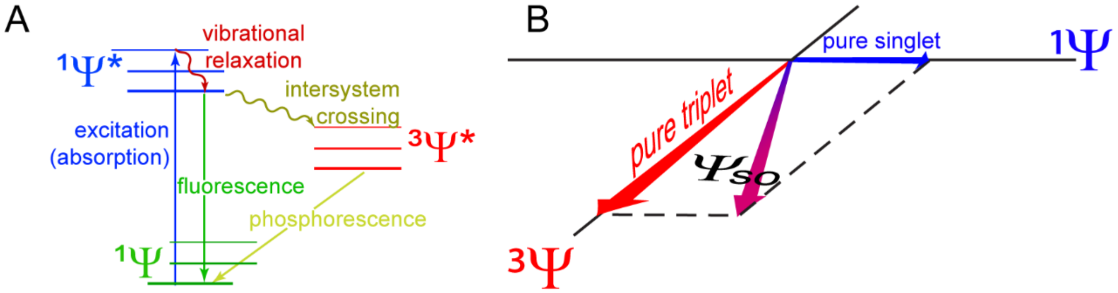


Figure 15.10. A. A Jablonski diagram of excited state dynamics. **B.** Spin-orbit coupling results in a mixing of singlet and triplet states. This allows for intersystem crossing and phosphorescece from the excited states of atoms and molecules.

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.

Conclusions.

References.

1. L. M. Haffner *et al* 2003 *ApJS* **149** 405.

Appendix. Coulomb and exchange integrals of singlet and triplet states.

Triplets. A triplet wavefunction is defined by the Slater determinate: $\Psi^3(1,2) =$

$$\det\frac{1}{\sqrt{2}}\begin{vmatrix}\Psi_1(1)\alpha(1) & \Psi_1(2)\alpha(2)\\ \Psi_2(1)\alpha(1) & \Psi_2(2)\alpha(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\Psi_1(1)\alpha(1)\Psi_2(2)\alpha(2) - \frac{1}{\sqrt{2}}\Psi_2(1)\alpha(1)\Psi_1(2)\alpha(2)$$

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ as follows:

$$\int \Psi^3(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^3(1,2)\cdot\partial\tau =$$

$$\int\{\psi_1^*(1)\alpha^*(1)\psi_2^*(2)\alpha^*(2) - \psi_2^*(1)\alpha^*(1)\psi_1^*(2)\alpha^*(2)\}\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\{\Psi_1(1)\alpha(1)\Psi_2(2)\alpha(2) - \Psi_2(1)\alpha(1)\Psi_1(2)\alpha(2)\}\cdot\partial\tau$$

Next the expression is FOIL'ed out and the spin wavefunctions are factored out:

$$\begin{aligned}\frac{1}{2}\int \psi_1^*(1)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\psi_2^*(2)\Psi_2(2)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\\ +\frac{1}{2}\int \Psi_1^*(2)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\Psi_2(1)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\\ -\frac{1}{2}\int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\\ -\frac{1}{2}\int \Psi_1^*(2)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\Psi_2(2)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\end{aligned}$$

Since $\int \alpha^*\,\alpha = 1$ and $\Psi_1^*(1)\Psi_1(1) = |\Psi_1(1)|^2$ etc., the above can be factored into:

$$\begin{aligned}\frac{1}{2}\left(\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int|\Psi_1(2)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(1)|^2\cdot\partial\tau\right)\\ -\frac{1}{2}\left(\int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau\right.\\ \left.+\int \Psi_1^*(2)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\Psi_2(2)\cdot\partial\tau\right)\end{aligned}$$

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:

$$\int \Psi^3(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^3(1,2)\cdot\partial\tau =$$

$$\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau - \int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau$$

Singlets: A singlet wavefunction is defined by two Slater determinates:

$$det\frac{1}{2}\left(\begin{vmatrix}\Psi_1(1)\alpha(1) & \Psi_1(2)\alpha(2)\\ \Psi_2(1)\beta(1) & \Psi_2(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\Psi_1(1)\beta(1) & \Psi_1(2)\beta(2)\\ \Psi_2(1)\alpha(1) & \Psi_2(2)\alpha(2)\end{vmatrix}\right)$$

$$=\frac{1}{2}\Psi_1(1)\alpha(1)\Psi_2(2)\beta(2)-\frac{1}{2}\Psi_2(1)\beta(1)\Psi_1(2)\alpha(2)-\frac{1}{2}\Psi_1(1)\beta(1)\Psi_2(2)\alpha(2)+\frac{1}{2}\Psi_2(1)\alpha(1)\Psi_1(2)\beta(2)$$

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ as:

$$\int \Psi^1(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^1(1,2)\cdot\partial\tau$$

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 $\psi_1^*(1)\Psi_1(1) = |\Psi_1(1)|^2$ etc., half the terms can be removed, and the remainder factored into:

$$\frac{1}{2}\left(\int |\Psi_1(1)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int |\Psi_1(2)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(1)|^2\cdot\partial\tau\right)$$
$$+\frac{1}{2}\left(\int \psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\psi_2^*(2)\Psi_2(1)\cdot\partial\tau\right.$$
$$\left.+\int \psi_1^*(2)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\psi_2^*(1)\Psi_2(2)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary. Thus, we have the Coulomb integral plus the exchange integral:

$\int \Psi^1(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^1(1,2)\cdot\partial\tau=$

$$\int |\Psi_1(1)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau$$

which proves that the paramagnetic triplet state is lower in energy than the singlet.

$$\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)$$

$$\begin{aligned}
&-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
&-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
&+\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)\\
&-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
&+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
&+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
&-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
&-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
&+\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
&+\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
&-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
&+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)\\
&-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
&-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
&+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\,\frac{\mathrm{e}^2}{4\pi\varepsilon_0|\mathrm{r}_1-\mathrm{r}_2|}\,\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)
\end{aligned}$$

Problems: Numerical

1. Shielding. While I once calculated $\langle r \rangle_{2s} = 6a_0$ and $\langle r \rangle_{2p} = 5a_0$ for a *1-electron* hydrogen atom, it is still true that the 2s electron is much closer to the nucleus, such that in a *multielectron* atom the 2s orbital is at a lower energy than a 2p orbital. Let's confirm that this is the case.

a. Calculate $|\psi(r)|^2$over a shorter range of distance, say 0 → a_0. First, start with the 2s wavefunction:

$$\psi_{2s}(r) = \frac{1}{(2\cdot a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)\cdot e^{-r/2a_0}$$

and evaluate $\int_0^{a_0}\psi_{2s}^*\cdot\psi_{2s}\cdot 4\pi r^2\cdot\partial r$ using Mathematica online:

http://www.wolframalpha.com/widgets/gallery/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605

Note that it is sometimes hard to write an equation such that Mathematica "likes" it: try this: x*x*(2-x/a)*(2-x/a)*exp(-x/a) dx. Use the limits 0 to a; note that a = a_0. And if you see the letter "e", that's exp(1)=2.71828… ***Hint:*** your answer should be a finite number like 0.4312, so don't forget all the constants especially the normalizer! Also if the website hangs just hit that equal sign to the lower right side of the box. **(8 pts)**

b. Now do the same for the 2p wavefunction:

$$\psi_{2p}(r) = \frac{1}{\sqrt{24}\cdot a_0^{5/2}}r\cdot e^{-r/2a_0}$$

to find: $\int_0^{a_0}\psi_{2p}^*\cdot\psi_{2p}\cdot 4\pi r^2\cdot\partial r$. **(8 pts)**

c. So, you see that in fact the 2s electron is more likely to be within 0 →a_0 of the nucleus by a factor of ~9.4× compared to the 2p, which is why multielectron atoms have lower energy 2s orbitals despite the fact that 2s and 2p are degenerate in 1-electron hydrogen atoms. Did you notice how this isn't a question?

( **pts)**

2. The Advanced Photon Source at Argonne National Lab is a huge facility that produces X-rays via Bremsstrahlung. It must generate a lot of X-ray power, right? For example, a nuclear power plant generates ~500 MW (megaWatts, or 500 Joules per second).

a. Let's say that the electrons circulate at a current of 1 nC ($= 1\times10^{-9}$C). How many electrons is that? **(4 pts)**

b. Now if the electrons (charge of an electron $= 1.6\times10^{-19}$ C) are accelerated to the speed of light ($= 3\times10^{8}$m/s) in 1.5 ps ($= 1.5\times10^{-12}$s), how much X-ray power is generated by the APS's electron beam? ***Hint:*** you need to use the Larmor formula for the power generated by a single, accelerating charge: $P = \frac{e^2a^2}{6\pi\mathcal{E}_0\cdot c^3}$, where e is the charge of an electron, a is the acceleration, and the permittivity of free space is: $\mathcal{E}_0 = 8.85\times10^{-12}\,\frac{s^4A^2}{kgm^3}$.

(6 pts)

c. A typical result is ~1 mW power. Did you get a much smaller value? In that case you may have forgotten to multiply the Larmor formula by the number of electrons. **(**  **pts)**

3. Absorption of light is not instantaneous- if it was, then there would be no conservation of energy or momentum. The timescale of absorption can be estimated from the time-energy uncertainty principal: $\Delta t \cdot \Delta E = \frac{1}{2}\hbar$. Try to calculate how much time it takes to absorb radiation for the following wavelength ranges (wavelengths given in parentheses):

a. Microwave (rotational, 10^{-1} m) **b.** Infra-Red (vibrational, 5×10^{-6} m)

c. Visible (electronic, 5×10^{-7} m) **d.** X-ray (core electronic, 1×10^{-9} m) **(8 pts)**

Hint: Estimate the uncertainty in the energy of the transition as being the same as the energy of light driving the transition itself.

Problems: Theoretical or Explain in Words

1. a. There is a branch of quantum mechanics called matrix mechanics. This is due to the fact that you can have eigenvalue equations in matrix form. Let's say that we have an operator: $\widehat{\Omega} = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}$ and an eigenfunction of that operator: $\Phi = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$. Can you show that:

$$\widehat{\Omega}\Phi = \omega\Phi$$

where $\omega = 0.9$? ***Hint:*** you might have to look up how to multiply a matrix by a column vector in Google. Also here is a useful identity: $\begin{bmatrix} -\omega \cdot a \\ \omega \cdot a \end{bmatrix} = \omega \begin{bmatrix} -a \\ a \end{bmatrix}$. **(3 pts)**

b. The eigenvalue equation $\widehat{\Omega}\Phi = \omega\Phi$ can be expressed as:

$$(\widehat{\Omega} - \omega)\Phi = 0$$

Such that, as in the previous example:

$$\widehat{\Omega} - \omega = \begin{bmatrix} 1-\omega & 0.1 \\ 0.1 & 1-\omega \end{bmatrix}$$

There is a theorem in mathematics that the eigenvalues ω of $\widehat{\Omega}\Phi = \omega\Phi$ can be found by:

$$det(\widehat{\Omega} - \omega) = 0$$

where det is the determinant. Can you show that solving:

$$det\begin{bmatrix} 1-\omega & 0.1 \\ 0.1 & 1-\omega \end{bmatrix} = 0$$

for ω provides a quadratic equation for ω? ***Hint:*** $det\begin{bmatrix} a & b \\ c & d \end{bmatrix} = ad - cb$. **(5 pts)**

c. Now if you solve the quadratic equation for ω in pt. b yields two eigenvalues, one of which is 0.9 as in pt. a. What is the other one? Hint: the roots of a quadratic equation: $ax^2 + bc + c = 0$ are $\frac{-b\pm\sqrt{b^2-4ac}}{2a}$. **(5 pts)**

d. Can you show that the eigenfunction $\Phi = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$ of $\widehat{\Omega} = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}$ has an eigenvalue $\omega = 1.1$? **(3 pts)**

2. a. In the previous problem set you found that a hydrogen atom in the 1s ground state has a turning point, just like the harmonic oscillator (in case you forgot the turning point is where the potential energy is equal to the kinetic energy, and beyond the turning point you must technically have negative kinetic energy).

a. Now let's calculate r_{tp} for the 2p state. We start with the following expression:

$$\frac{h^2}{8\pi^2 m \cdot {r_{tp}}^2} l(l+1) - \frac{e^2}{4\pi\varepsilon_0 \cdot r_{tp}} = -\frac{m \cdot e^4}{32\varepsilon_0^2 \cdot h^2}$$

Hint: The Wolfram website has a facility to solve for a variable:

https://www.wolframalpha.com/widgets/view.jsp?id=c778a2d8bf30ef1d3c2d6bc5696defad

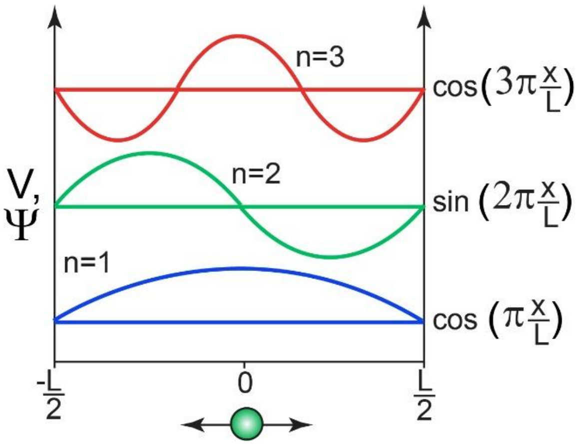
You need to input something that Wolfram understands, so I had to use some codes like:

f= e, h= h, o=ε_0, and pi= π. I then input: h^2/4/pi^2/m/x^2-f^2/4/pi/o/x=-m*f^4/32/o^2/h^2. **(5 pts)**

b. In pt. a you got two answers. One, at a large distance, is slightly less than the 2s value. This makes sense because the 2p has a small amount of angular kinetic energy, so it has less total energy to use to stretch further from the nucleus compared to the 2s.

However, you found another turning point at a shorter distance: $\left(\frac{1.17}{\pi}\right)\frac{\varepsilon_0 h^2}{m \cdot e^2}$. Can you explain this one? ***Hint:*** Do you recall why p- and d- orbitals have an $\psi \sim r^l$ term in the wavefunctions? Something about not getting to close to the nucleus? Maybe this will help: https://www.youtube.com/watch?v=0RVyhd3E9hY **(4 pts)**

3. Let's do some model calculations on spectroscopic transition moments using particle in a box wavefunctions instead of the H-atom, mostly because that is way easier. In this problem we will use the centered box form as shown here:



a. Let's evaluate some transition moments. Assuming particle-in-a-box wavefunctions as shown in the figure, what is the correct expression to calculate the transition moment for the ground state to the 1st excited state? For the 2nd excited state? **(2 pts)**

b. Now use the Wolfram symbolic integrator to evaluate: **(6 pts)**

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \cdot (-e \cdot \hat{x}) \cdot \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) \cdot \partial x$$

and:

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \sqrt{\frac{2}{L}} \cos\left(\frac{3\pi x}{L}\right) \cdot (-e \cdot \hat{x}) \cdot \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) \cdot \partial x$$

c. Based from the results in pt. a, can you designate a □n transition rule, where n is the quantum number for the particle in a box? Hint: n=1 for the ground state, n=2 for the 1st excited state, … **(2 pts)**

4. a. You can often see spectroscopic transitions from the ground state to highly excited states. For example, for the particle in a box, can you show that the transition moment of the ground → 3th excited state is not 0 but is much weaker than for the ground → 1st excited state? **(4 pts)**

b. How much weaker is the ground → 3th excited state and ground → 5th excited state transition comparted to ground to 1st from question 4b? **(4 pts)**

5. Let's repeat the exercises of question 4 with vibrational wavefunctions!

Assuming the ground state is: $\psi_{\upsilon=0} = \left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} \cdot e^{-x^2/2\alpha^2}$ and excited state is:

$\psi_{\upsilon=1} = \left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} \left(\frac{2x}{\alpha}\right) \cdot e^{-x^2/2\alpha^2}$. As a result, the transition moment is:

$$\int_{-\infty}^{\infty} \left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} \left(\frac{2x}{\alpha}\right) \cdot e^{-x^2/2\alpha^2} \cdot (-e \cdot \hat{x}) \cdot \left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} \cdot e^{-x^2/2\alpha^2}\, \partial x$$

a. Note that I haven't asked a question yet- here it is- can you simplify the above expression into the simplest form and then evaluate whether the integral is 0 or not? Basically, just factor out constants and see what you have left, and then evaluate by any means whether the integral is 0 or not (don't worry about determining a value, just answer if it is 0 or not). **(4 pts)**

b. Now try the same thing with the ground to 2nd excited state:

$\psi_{\upsilon=2} = \left(\frac{1}{4\alpha\pi^{1/2}}\right)^{1/2} \left(\frac{4x^2}{\alpha^2} - 2\right) e^{-x^2/2\alpha^2}$ **(4 pts)**

Hint: You should be able to simplify the expressions a lot and find the proper identities at the beginning of this problem set.

6. a. Let's start simple- what do you get when you integrate the absolute value of a normalized radial wavefunction $\left|\Psi_{n=1,l=0}(r)\right|^2$ for a hydrogen atom with a single electron (1s^1 state)?

Hint: solve this:

$$\int |\Psi|^2 = \int_0^{\infty} \Psi^*(r) \cdot \Psi(r) \cdot \partial\tau = \int_0^{\infty} \left(\frac{2}{(a_0)^{3/2}} e^{-r/a_0}\right)^* \cdot \frac{2}{(a_0)^{3/2}} e^{-r/a_0} \cdot r^2 \cdot \partial r$$

You should know the answer, ***you don't have to do any math if you explain yourself***. **(2 pts)**

b. Now we will try to construct a multielectron wavefunction- let's work on a negative hydrogen with two electrons in the 1s state (the 1s^2 configuration). Our first try for writing the wavefunction is:

$$\Psi = \Psi_{1s}(r_1) \cdot \Psi_{1s}(r_2)$$

We will now calculate the integrated absolute value:

$$\int |\Psi|^2 = \int_0^{\infty}\int_0^{\infty} \Psi_{1s}^*(r_1)\Psi_{1s}^*(r_2) \cdot \Psi_{1s}(r_1) \cdot \Psi_{1s}(r_2) \cdot r_1^2 \cdot \partial r_1 \cdot r_2^2 \cdot \partial r_2 =$$

$$\int_0^{\infty}\int_0^{\infty} \frac{4}{a_0^3} r_1^2 \cdot e^{-2r_1/a_0} \cdot \frac{4}{a_0^3} r_2^2 \cdot e^{-2r_2/a_0} \cdot \partial r_1 \cdot \partial r_2$$

Tell me what this double integral is equal to. Hint: you can evaluate them separately and then multiply the results ala: $\left(\int_0^{\infty} \frac{4r_1^2}{a_0^3} \cdot e^{-2r_1/a_0} \cdot \partial r_1\right) \cdot \left(\int_0^{\infty} \frac{4r_2^2}{a_0^3} \cdot e^{-2r_2/a_0} \cdot \partial r_2\right)$ **(4 pts)**

c. In actuality the result of "1.0" in pt. b is bad. While it appears that the wavefunction is properly normalized (good), it is also true that the two electrons are in the same state at the same time if they have the same spin. In this Universe this is impossible!

It must be true that, for two electrons in the same state: $\int |\Psi|^2 = 0$!

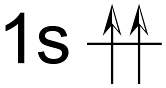
Here is our first attempt to fix this problem- we introduce spin wavefunctions α and β.

The spin wavefunctions only have the following properties:

$\int \alpha^* \cdot \alpha = \int \beta^* \cdot \beta = 1$ and $\int \alpha^* \cdot \beta = \int \beta^* \cdot \alpha = 0$ and $\alpha = \alpha^*, \beta = \beta^*$

Now for our example of a hydrogen anion $1s^2$ state Let's make both electrons spin up:

$$\Psi = \Psi_{1s}(r_1)\alpha(1) \cdot \Psi_{1s}(r_2)\alpha(2)$$



Now the integrated absolute value is:

$$\int|\Psi|^2 = \int_0^\infty \int_0^\infty \Psi_1^*(r_1)\Psi_1^*(r_2) \cdot \Psi_1(r_1)\Psi_1(r_2) \cdot 4\pi r_1^2 \cdot \partial r_1 \cdot 4\pi r_2^2 \cdot \partial r_2 \cdot \{\int \alpha^*(1)\alpha(1) \cdot \int \alpha^*(2)\alpha(2)\}$$

What does $\int|\Psi|^2$ above equal to (and explain your answer!)? **(2 pts)**

Hint: You have to evaluate two integrals of spin, and you still don't get 0!

7. Question 6c was screwed up- the wavefunction integrated to 1.0 even though the electrons were in the same state! This should not have happened!

Now here is the fix- you make the ***multielectron wavefunction itself equal to 0*** if both electrons are in the same state. The proper way to make this happen is to have the wavefunction be antisymmetric to interchange:

$$\Psi(1,2) = -\Psi(2,1)$$

Now how do you do this? Here is an example- first we start with a not-quite-right $1s^2$ spinup-spindown wavefunction: $\Psi = \Psi_{1s}(r_2)\beta(2) \cdot \Psi_{1s}(r_1)\alpha(1)$ and transform it into the proper antisymmetric form that you saw in class:

$$\Psi = \left\{\frac{\Psi_{1s}(r_1) \cdot \Psi_{1s}(r_2) + \Psi_{1s}(r_2) \cdot \Psi_{1s}(r_1)}{\sqrt{2}}\right\}\left\{\frac{\beta(1)\alpha(2) - \beta(2)\alpha(1)}{\sqrt{2}}\right\}$$

a. Can you show that $\Psi(1,2) = -\Psi(2,1)$? Hint, it happens in the "spin" part. **(4 pts)**

b. Can you now show that $\int|\Psi|^2 = 1$? You can just do the spin part, the space part:

$\iint \left|\frac{\Psi_{1s}(r_1)\cdot\Psi_{1s}(r_2)+\Psi_{1s}(r_2)\cdot\Psi_{1s}(r_1)}{\sqrt{2}}\right|^2 \cdot \partial\tau_1\partial\tau_2 = 1.0$. So you just have to do the spin part:

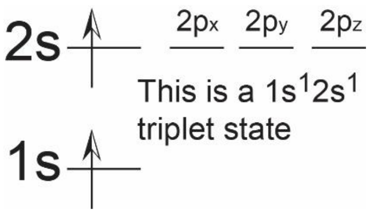
$$\frac{1}{2}\iint \{\beta(1)\alpha(2) - \beta(2)\alpha(1)\}^* \cdot \{\beta(1)\alpha(2) - \beta(2)\alpha(1)\}$$

Recall that spin identities are at the top of this page. **(8 pts)**

Hint: if you need to integrate something like this: $\iint \beta^2(2)\alpha^2(1)$, you divvy up the integrals between electrons 1 and 2 as so: $\int \beta^2(2) \cdot \int \alpha^2(1)$. This is $1 \cdot 1 = 1$.

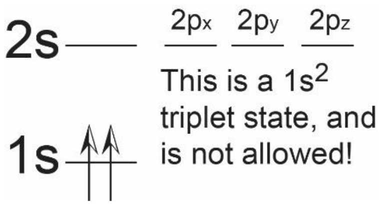
c. If the system had both electrons spin up, can you show that $\Psi = 0$? **(2 pts)**

8. The example in question 9 was for a singlet state, which use spin wavefunctions to impart the antisymmetry property. For triplets, the "space" wavefunctions are used to enforce the antisymmetry property. For example, the proper antisymmetric wavefunction for a $1s^1 2s^1$ spinup-spinup configuration is:



$$\Psi(1,2) = \left\{\frac{\Psi_{2s}(r_1)\Psi_{1s}(r_2) - \Psi_{2s}(r_2)\Psi_{1s}(r_1)}{\sqrt{2}}\right\}\alpha(1)\alpha(2)$$

a. Let's see what happens if the two electrons are in the same state as shown here (a $1s^2$ triplet, which is impossible). Please write out the correct wavefunction and show that $\Psi = 0$. Hint: just write out $\Psi(1,2)$ above and make every "Ψ_{2s}" a "Ψ_{1s}". **(4 pts)**



b. We can't make the spin wavefunctions symmetric if the space part is. As a result, there are three potential spin wavefunctions: $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$ and a weird one: $\frac{\beta(1)\alpha(2)+\beta(2)\alpha(1)}{\sqrt{2}}$. **(6 pts)**

Can you show that the spin parts of $\int |\Psi_{spin}|^2$ for $\frac{\beta(1)\alpha(2)+\beta(2)\alpha(1)}{\sqrt{2}}$ integrates to 1.0? To assist you, I have done an example for $\alpha(2)\alpha(1)$:

$$\int |\Psi_{spin}|^2 = \int\int \{\alpha(2)\alpha(1)\}^* \cdot \alpha(2)\alpha(1) = \{\int \alpha^*(2)\alpha(2)\} \cdot \{\int \alpha^*(1)\alpha(1)\} = 1.0 \cdot 1.0 = 1.0$$

2. Recall from the last problem set that you learned a bit about quantum mechanics and matrices. Here we will see how molecular orbitals are calculated from the matrix method.

a. If a H atom in its $1s^1$ ground state is infinitely far away from another ground state H atom, then there is no interaction, and the Hamiltonian matrix is:

$$\hat{H} = \begin{array}{ccc} & H(1)_{1s} & H(2)_{1s} \\ H(1)_{1s} & E_{1s} & 0 \\ H(2)_{1s} & 0 & E_{1s} \end{array}$$

where $H(1)_{1s}$ represents the first H atom 1s state, $H(2)_{1s}$ represents the second H atom's 1s state, and E_{1s} is the energy of an H atom's 1s orbital. Please determine the eigenvalues of $\hat{H}$ using the on-line eigenvalue calculator from Wolfram. The input for a matrix such as $\begin{bmatrix} a & -b \\ 0 & c \end{bmatrix}$ would be {{a,-b},{0,c}}, and it calls the eigenvalues l. You also have to use letters for the matrix or the website won't work, so you should insert "E_{1s}" as "a". **(3 pts)**

b. Now if the H atoms get closer together they will have an interaction energy ϵ. Thus the Hamiltonian matrix is now:

$$\hat{H} = \begin{array}{ccc} & H(1)_{1s} & H(2)_{1s} \\ H(1)_{1s} & E_{1s} & -\epsilon \\ H(2)_{1s} & -\epsilon & E_{1s} \end{array}$$

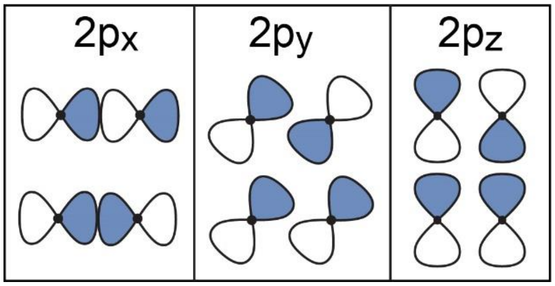
There is a negative sign in: $-\epsilon$ is because the interaction energy is attractive or "downhill". What are the eigenvalues of this matrix, and how do you interpret the results? **(5 pts)**

Answer: a. You plug into the website something like this: {{a,0},{0,a}}. The resulting eigenvalues are both $l_{1,2}$="a"=E_{1s}, meaning that there is no interaction and the energies of the H atoms haven't changed at all.

b. You plug into the website something like this: {{a,-b},{-b,a}}, and the resulting eigenvalues are:

l_1="a-b"=E_{1s}- ϵ, which is the bonding s-s orbital.

l_2="a+b"=$E_{2p}+\epsilon$, which is the antibonding s-s orbital.



3. Now we will create the Hamiltonian matrix for an oxygen atom's p-orbitals when interacting with another O atom's p orbitals. Shown here are the bonding and antibonding configurations of the p_x, p_y and p_z orbitals between two oxygen atoms. You should note that the p_x orbital's interactions are different than the p_y and p_z, as the p_xs' appears "stronger" due to the greater overlap (i.e. the two p_x interact "head-to-head", forming s-type bonds, whereas the others appear "side-to-side" and form p-type bonds).

The Hamiltonian matrix is:

$$\hat{H} = \begin{array}{c} \\ H(1)_{2px} \\ H(1)_{2py} \\ H(1)_{2pz} \\ H(2)_{2px} \\ H(2)_{2py} \\ H(2)_{2pz} \end{array} \begin{array}{c} \begin{array}{cccccc} H(1)_{2px} & H(1)_{2py} & H(1)_{2pz} & H(2)_{2px} & H(2)_{2py} & H(2)_{2pz} \end{array} \\ \begin{bmatrix} E_{2p} & 0 & 0 & -\epsilon_2 & 0 & 0 \\ 0 & E_{2p} & 0 & 0 & -\epsilon_1 & 0 \\ 0 & 0 & E_{2p} & 0 & 0 & -\epsilon_1 \\ -\epsilon_2 & 0 & 0 & E_{2p} & 0 & 0 \\ 0 & -\epsilon_1 & 0 & 0 & E_{2p} & 0 \\ 0 & 0 & -\epsilon_1 & 0 & 0 & E_{2p} \end{bmatrix} \end{array}$$

a. Using the Wolfram website, what are the eigenvalues of this matrix? How do you interpret each one? ***Hint:*** obviously, there are 6 of them. Likely they represent boding and antibonding orbitals comprised of p_x, p_y and p_z orbitals. **(8 pts)**

b. Can you draw a MO diagram from the results? Also, please occupy the molecular orbitals with the 8 total electrons. Is oxygen a singlet or triplet? ***Hint:*** ϵ_2 is greater than ϵ_1. **(8 pts)**

Answer: a. You plug into the website something like this:

{{a,0,0,-b,0,0},{0,a,0,0,-c,0},{0,0,a,0,0,-c},{-b,0,0,a,0,0},{0,-c,0,0,a,0},{0,0,-c,0,0,a}}

And the eigenvalues are:

l_1 $E_{2p}-\epsilon_2$, which is the bonding p_x-p_x orbital.

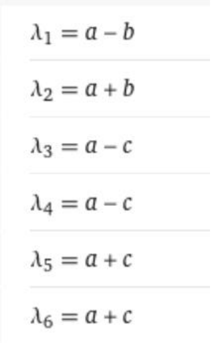
l_2 $E_{2p}+\epsilon_2$, which is the antibonding p_x-p_x orbital.

l_3 $E_{2p}-\epsilon_1$, which is the bonding p_y-p_y or p_z-p_z orbital.

l_4 $E_{2p}-\epsilon_1$, which is the bonding p_y-p_y or p_z-p_z orbital.

l_5 $E_{2p}+\epsilon_1$, which is the antibonding p_y-p_y or p_z-p_z orbital.

l_6 $E_{2p}+\epsilon_1$, which is the antibonding p_y-p_y or p_z-p_z orbital.



$\lambda_1 = a - b$

$\lambda_2 = a + b$

$\lambda_3 = a - c$

$\lambda_4 = a - c$

$\lambda_5 = a + c$

$\lambda_6 = a + c$

b. The eigenvalues are such that the bonding p_x-p_x bonding orbital is on bottom, followed by degenerate p_y-p_y and p_z-p_z bonding, and next p_y-p_y and p_z-p_z antibonding and p_x-p_x antibonding on top. Since there are 8 total electrons you get the following configuration which is clearly a triplet.